Sol−Gel Materials in Electrochemistry

O. Lev,* Z. Wu, S. Bharathi, V. Glezer, A. Modestov, J. Gun, L. Rabinovich, and S. Sampath

Laboratory of Environmental Chemistry, Division of Environmental Sciences, Fredy and Nadine Herrmann School of Applied Science, The Hebrew University of Jerusalem, Jerusalem, 91904 Israel

Received May 16, 1997. Revised Manuscript Received September 15, 1997[⊗]

The subject of sol−gel electrochemistry is introduced, starting with a brief account of milestones in its evolution. Then, the types of sol−gel materials that are useful for electrochemistry are presented, followed by a description of recent advances in the various fields of sol−gel electrochemistry. Modified electrodes, solid electrolytes, electrochromic devices, and corrosion protection coatings are described. Emerging fields such as RuO_2 supercapacitors and electrochemical synthesis of sol−gel precursors are also addressed.

1. Introduction

Sol−gel is gradually attracting the attention of the electrochemical community as a versatile way for the preparation of modified electrodes and solid electrolytes. The subject of sol−gel electrochemistry is introduced here, starting with a brief account of milestones in its evolution. Then the types of sol−gel materials that are useful for electrochemistry are presented, followed by a description of recent advances in the various fields of sol−gel electrochemistry. Modified electrodes, solid electrolytes, electrochromic devices, and corrosion protection coatings are described. Other fields that are still dominated by only a few research groups but have promising prospects such as electrochemical probing of sol−gel processing, recent advances in supercapacitors, and electrochemical methods for synthesis of sol−gel precursors are also addressed. However, the fields of photoelectrochemistry and rechargeable lithium batteries require different scientific introductions and are not addressed here.

The terminology "sol−gel" is used to describe a broad class of processes in which a solid phase is formed through gelation of a colloidal suspension (sol). Drying of the gel can then give the "dry gel" (xerogel) state and subsequent heat treatment can be used to remove unreacted organic residues, stabilize the gel, densify it, or introduce crystallinity.[1−4] The terminology, which was initially reserved for the production of metal and semimetal oxides, was gradually extended to include preparation of organic−inorganic hybrids,[5−7] and occasionally it is even used to describe the production of pure organic networks (e.g., resorcinol−formamide polycondensation process[8]).

Historical Perspective. The first record of sol−gel processing is attributed to J. Ebelmen, a French scientist who described as early as 1846 the synthesis of silicate monoliths from a tetraethoxysilane precursor (made from tetrachlorosilane and ethanol).[9] In 1885 another French scientist, A. Ditte, described a sol−gel process for the formation of vanadium pentoxide.[10] However, modern concepts of sol−gel science agglomerated only during the past few decades. At first, scientific interest centered on the favorable optical characteristics of silica, zirconia, and other transparent oxides. Since 1980, the technology became attractive to the electrochemical community as well. Initially, electrochemists were interested in sol−gel technology as a convenient method to intimately mix different metal oxides en route to the production of crystalline materials. In many cases xerogels made of dissolved precursors could be sintered at lower temperatures as compared to conventional methods, starting from mixture of powders. This was the motivation for the synthesis of sol−gel derived nasicons (sodium super ion conductors), which were first reported in 1980 by Quon et al.[11] In 1984 Livage and co-workers[12] synthesized sol−gel tungsten oxide for electrochromic applications, and in 1986 Yoko et al. introduced sol−gel derived titanium dioxide electrodes for photoelectrochemical splitting of water.[13] This was almost 2 decades after the first report on semiconductor photoelectrochemistry.[14] In view of the current popularity of sol−gel derived semiconductive materials, it now looks surprising that the importance of sol−gel photoelectrochemistry was realized so late, especially, since $SiO_2−TiO_2$ antireflecting windows were already commercially available by then.[15]

During the past decade amorphous sol−gel materials have become more appealing to the electrochemical community. Xerogels, aerogels, and even conductive hydrous gel applications have materialized. It is now well accepted that amorphous materials function much better than their crystalline counterparts in some applications, especially those requiring fast diffusion, such as lithium intercalation batteries,[16,17] supercapacitor electrodes,[18] and solid electrolytes.[19] Concurrently, organic−inorganic hybrids have emerged as versatile electrode and electrolyte materials.[16]

Murray and co-workers[21−24] were the first to apply redox modified siloxane-based cross-linked films on silicon, platinum, and other metal electrodes. Monolayers and thin films based on trichloro- or trimethoxyaminosilanes were first coated, and redox spe-

---

[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1997.

cies were then anchored onto the preprepared layers. Although the original intention was to modify the electrodes with a monolayer of redox modifiers, a thin cross-linked polymer coating was often observed.[20,24] Later, Wrighton and co-workers applied chloro- or ethoxysilylferrocene modifiers on inert metals and n-type semiconductors.[25−27] Since it is likely that film formation in Wrighton's and Murray's studies were preceded by polycondensation and sol formation, these studies can be regarded as the first electrochemical investigations of sol−gel derived materials, though the terminology sol−gel was never mentioned in these studies.

To conclude this subjective historical overview, two seminal papers that appeared in 1984 should be mentioned. The papers introduced novel ways to incorporate organic moieties in xerogels and they had a profound effect on contemporary sol−gel electrochemistry. Philipp and Schmidt[28] exploited the fact that Si−C bonds are very stable and do not hydrolyze during sol−gel processing in order to develop the organically modified ceramic (ormocers) and silicate (ormosil) materials, using organofunctional silane precursors such as meythyltrimethoxysilane, MTMOS. Avnir et al.[29] showed that it is possible to immobilize organic compounds in xerogels by mixing them with the sol−gel precursors. These two methods opened new avenues to combine the superior physical properties of inorganic materials with the large variety of organic compounds.

Sol−Gel Electrolyte and Electrode Materials. From the "material science" point of view, the following four classes of material compositions are used in sol−gel electrochemistry in their hydrous gel, xerogel, or crystalline form.

1. Inert, inorganic materials: Silica, alumina, and zirconia xerogels are frequently used by electrochemists. The metal atom of these compounds has only one relevant stable oxidation state, and the materials do not undergo redox reactions in aqueous solutions. Still, the large surface area of gels, their large specific ion-exchange capacity, contributed by surface hydroxyls, and their good adhesion to metal oxides and ceramic supports make them attractive for specific electrochemical applications, especially in the fields of corrosion protection coatings (discussed in section 7)[30] and solid electrolytes (section 4).[19,31] Additionally, these materials are increasingly used as supports for electrochemically active species in modified electrodes (sections 2 and 3), which benefit from the rigidity, porosity, and electrochemical inertness of the xerogels. A notable limitation is the difficulty to prepare thick (>1 μm) sol−gel films. This, however, can be resolved by using multiple sol−gel coatings, by starting from aged or sonicated sols or by reducing the degree of cross-linkage, for example, by introduction of monomers containing a smaller number of hydrolyzable groups (e.g., di- and trialkoxysilanes).

2. Redox-active metal oxides: Tungsten oxide, vanadium pentoxide, manganese oxide, and most other transition-metal oxides exhibit several oxidation states, and their structure is sensitive to the redox state and the pH. The compositions of their precursors are also sensitive to these parameters, which can be manipulated to control the sol formation and gelation.[35,36] Electrochemical oxidation/reduction can cause coloration/discoloration (i.e., electrochromism) of some oxides and can accommodate reductive insertion of lithium and other molecules. These materials are useful for electrochromic devices (section 6) and battery applications. An important subgroup is the n-type semiconductive oxides (e.g., ZnO, $BaTiO_3$, TiO_2) which are extensively used for photosensitization in photovoltaic cells and other photoelectrochemical applications.

3. Organic−inorganic hybrids: Covalent bonding, sol−gel doping, impregnation, and intercalation are the methods used to modify inorganic gels by organic species.

3.1. Covalent bonding: Covalently bonded organic−inorganic hybrids benefit from the high stability of the carbon−silicon bond. Several general methods are used to form covalently bonded organic−inorganic hybrids.[32] Sol−gel monomers containing Si−C bonds can be used as sol−gel precursors. The Si−C bond does not participate in the sol−gel hydrolysis and polycondensation and the organo-functional groups remain exposed on the surface of xerogel. A second method is to derivatize the surface of preprepared gels by organic compounds containing reactive functional groups such as chloro- or alkoxysilanes. It is also possible to combine the two previous methods and to prepare gels containing an appropriate chemical anchor (e.g., by starting from aminosilane precursors) by the first method and then to attach a desirable organofunctional group onto the reactive anchor after gel formation. An important variant of this technology is the use of strong bidentate ligands, such as acetylacetone that bind irreversibly to some transition-metal alkoxides. The organo-functional group remains attached to the porous surface even after the formation of the xerogel.[33,34]

3.2. Sol−gel doping: Organic compounds can be incorporated into sol−gel materials by mixing with the starting sol−gel solution.[7] This technique is not limited to silicates and can be easily realized with other gels as well. It is useful for the encapsulation of large size catalysts or electrode modifiers, but it had only limited success in the encapsulation of charge mediators. Small charge mediators, particularly those that have little affinity to the gel surface, will leach out, while the mobility of bulky mediators will often not be sufficient for efficient charge shuttling between the surrounding environment and the electrode.

3.3. Impregnation: Adsorption or precipitation of organic compounds onto preprepared gels is the traditional method for organic modification of inert supports. Its success depends on the relative affinity of the modifier to the gel surface and its miscibility in the aqueous solution.

3.4. Intercalation compounds: Lack of crystallinity entails flexibility and promotes intercalation of organic compounds and ions. For some metal oxides (e.g., vanadium pentoxide) a hydrous layered structure is formed that can swell and accommodate intercalation of compounds with or without accompanied redox reaction. An important subclass of these materials was introduced by Kanatzidis et al.:[37] Layered materials of vanadium oxide and polyanilines or polyhetrocycle conducting polymers were produced by exposure of vanadium oxide gels to aniline, pyrrole, thiophene, and other monomers which are oxidized and polymerized between the vanadium oxide layers.

The large variety of the organic−inorganic hybrids makes them useful in many fields of electrochemistry, including sensing and biosensing, solid electrolytes, electrochromic devices, batteries, and photoelectrochemistry.

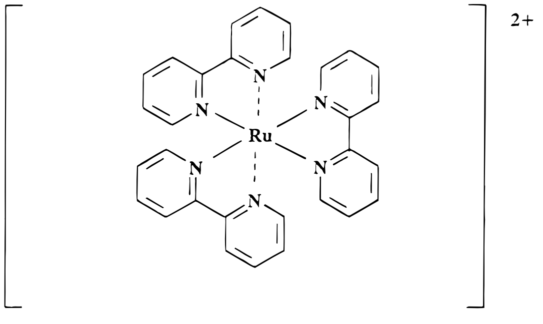
4. Macro- and microscopic composites: Sol–gel doping is not confined to the molecular level. Unicellular microorganisms, whole cells, and powders ranging in size from nanodimension to submillimeter level can also be encapsulated in sol–gel matrixes using the same methodology.[7] A dispersion of conductive powder can entail electron conductivity when its loading exceeds the percolation threshold level (e.g., graphite–silicate composites[38]). Another useful method to produce composites is by copolymerization of two oxides from the same sol. Dispersions of nanocrystalline materials in amorphous gels is now frequently used to combine the favorable properties of the surrounding amorphous gel and the crystalline active centers. Thus, for example, amorphous titania is used to improve lithium mobility toward crystalline ceria grains in ceria–titania films that are used as counter electrodes in electrochromic devices,[39] and porous silica and ormosils are used to improve the mobility and preconcentrate species in the vicinity of nanocrystalline titania photocatalysts.[40,41]

2. Modified Electrodes and Electrochemical Sensors

Sol–gel modified electrodes were demonstrated for diverse applications, including working electrodes, electrocatalysis, reference electrodes, and amperometric and potentiometric sensing and biosensing. Synthetic routes for the production of sol–gel modified electrodes, including ways to produce surface and bulk modified electrodes, redox and electron conducting polymers, and their possible use in electrochemical sensing are discussed in this section.

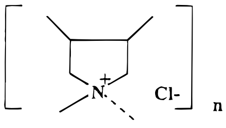
2.1. Surface-Modified Electrodes. A simple method to modify electrodes is to apply a thin sol–gel film containing the required reagent onto them. Charge mediators and chromophores, metal and organo-metallic catalysts, preconcentration agents, ionophores, and active proteins are used as electrode modifiers. The encapsulated modifiers can then interact with both the surrounding environment and the electrode surface. The different synthetic procedures that were used to modify electrodes and the methods to prevent leaching of the encapsulated reagents are discussed below.

Amperometric electrodes: Several groups studied the voltammetric response of film-coated electrodes.[42,44–47] Dvorak and Armond[42] exploited the favorable optical transparency of silicate films and demonstrated that the photoelectrochemical activity of tris(2,2′-bipyridyl)ruthenium (**1**) is retained in silicate films. The observed quantum yield was low, and diffusion characteristics were rather sluggish. This is commensurate with the low diffusion coefficients reported for organic compounds in tetramethoxysilane (TMOS) derived gels.[43]

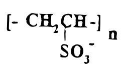


1

Several amperometric studies demonstrated ionic selectivity of silicate and ormosil coated electrodes.[44–47] Silicate films doped with bulky poly(dimethyldiallylammonium chloride) (**2**) and poly(vinylsulfonic acid) (**3**) charged dopants were used to concentrate the oppositely charged tris(2,2′-bipyridyl)ruthenium cation (**1**) and hexacyanoferrate anion, respectively.[44] Previous report showed leaching of small ion-exchange groups from sol–gel silicate materials,[45] but the bulky polymers used in this research did not leach at all from the membrane. The detection limit of the model compounds by square-wave voltammetry was improved by up to 50 times as compared to uncovered electrodes.[44] In fact, even a blank, undoped silicate film acted as an ion exchanger and concentrated the positively charged ion, (**1**) by the deprotonated, negatively charged surface silanol groups. Similar selectivity was recently reported for electrodes that were coated with a film prepared from (3-aminopropyl)methyldiethoxysilane.[46] A preliminary note describing a novel way to modify electrodes by coating with a delaminated Laponite clay sol and octakis(3-aminopropylsilasesquioxane) was recently published.[47] The selectivity of the electrodes toward cationic and anionic analytes (measured by CV) was inversed upon increasing the loading of the amine-containing oligomer in the composite film. The anionic properties of the clay dominated at low loading, while at higher dopant loading the positively charged amine groups became more dominant.



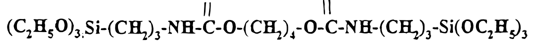
2



$[\text{-}\ CH_2\underset{SO_3^-}{CH}\text{-}]_n$

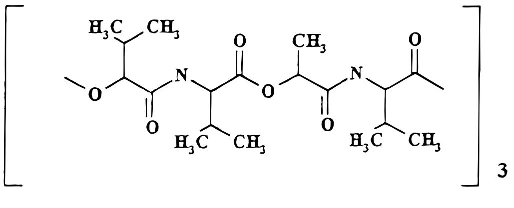
3

Potentiometric applications: Several potentiometric sol–gel electrodes were reported.[48–50] Kim et al.[48] synthesized sol–gel derived chloride-selective electrodes containing a chloride ionophore, tridodecylmethylammonium. The sol–gel membrane was comprised of a sol–gel copolymer made of TMOS and bis{ethylamidepropyl(triethoxysilane)} (**4**), which was prepared by condensation of (3-isocyanopropyl)triethoxysilane



$(C_2H_5O)_3Si\text{-}(CH_2)_3\text{-}NH\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}(CH_2)_4\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH\text{-}(CH_2)_3\text{-}Si(OC_2H_5)_3$

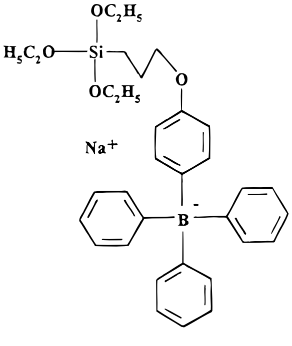
4



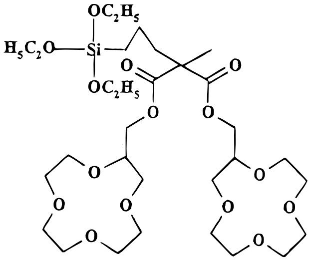
5

and 1,4-butanediol. The organic–inorganic composition prevented the leaching of ion-exchange compounds from the membrane. The sol–gel membrane was flexible and could be cut with a cork cutter and applied on a conventional Phillips electrode mount. The selectivity toward chloride over lipophilic anions was significantly improved as compared to organic membrane-coated electrodes, probably due to the negatively charged surface silanols.

Ion-selective membranes containing neutral carriers, valinomycin (**5**), and a 12-crown-4 derivative were synthesized for selective detection of potassium and sodium ions.[49] The membrane was used in an ISFET (ion-selective field effect transistor) configuration, and the detection range spanned over 10^{-6}–1.0 M for both ions. However, leaching of the reagents from the membranes drove the authors to use covalently bound reagents. The new membrane was prepared by copolymerization of tetraethoxysilane (TEOS), diethoxydimethylsilane, an ionic site (sodium triphenyl{4-[3-(triethoxysilyl)propoxy]phenyl}borate (**6**) and an alkoxysilyl-substituted crown ether derivative (bis(2,5,8,11-tetraoxacyclododecylmethyl)-2-[3-(triethoxysilyl)propyl]-2-methylmalonate (**7**). The chemically bonded reagents did not leach from the membrane and the detection range and sensitivity were similar to that obtained by the free crown-ether modified gels.[50]



6



7

The good adhesion of silicates to electrode surfaces, the favorable abrasion resistance, and good optical characteristics combined with versatility in tailoring hydrophobicity and affinity of the films make sol–gel modified electrodes promising electrochemical tools. Three methods are currently used to prevent leaching of reagents from the films: (1) Covalent bonding. This technique (e.g., ref 49) usually requires some organic synthesis efforts for the preparation of the organofunctional silane monomers or for the covalent bonding of the reagent to the supporting matrix. This is usually accompanied by a change in the formal potential of the electrode. The pro side of this technique includes the ability to provide zero leak electrodes. (2) Bulky dopants (e.g., refs 44 and 47). This technique relies on the encapsulation of polymers or other bulky reagents. Like covalent bonding it is restricted to cases where mobility of the encapsulated reagent can be compromised, and it requires synthesis capability in the preparation of the dopant. (3) Manipulation of the affinity of the supporting matrix to the encapsulated reagent. Appropriate selection of the organofunctional group on the ormosil can be used to enhance the partition coefficient of the dopant between the support and the electrolyte phase. Simplicity of the technique and only small variation of the formal potential of the dopant compared to its electrolyte-dissolved state are the major advantages of the technique. However, electrodes prepared by this technique are expected to exhibit some leakage under long periods of operation. A fourth method, control of the pore size distribution of the supporting matrix, was not employed yet in eletrochemical studies though it is widely used in sol–gel optical sensing applications.[7]

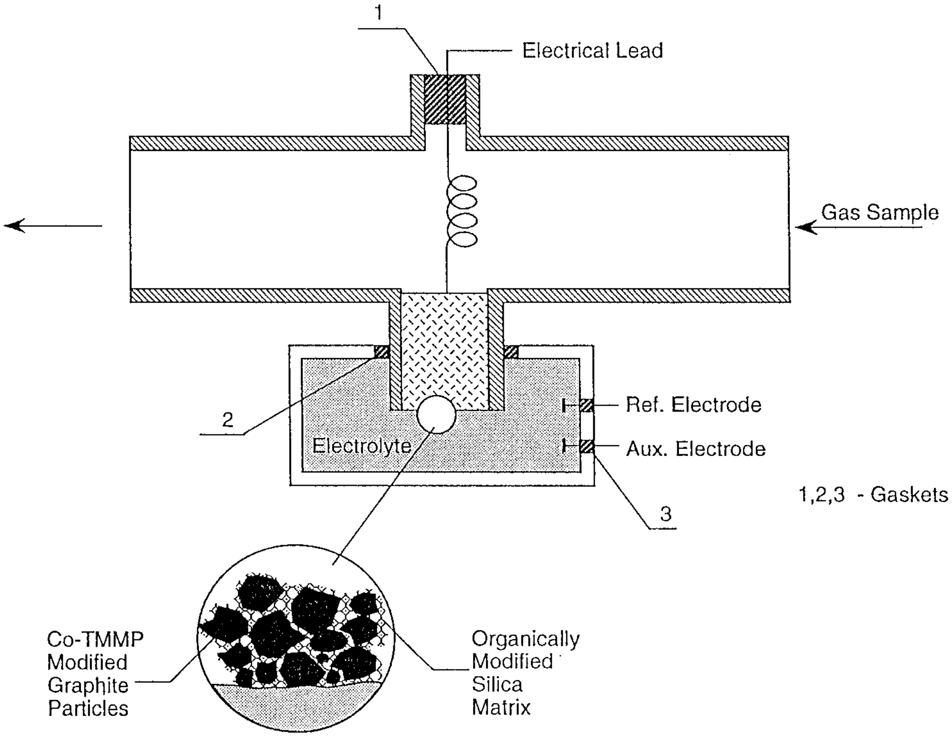
2.2. Ceramic–Carbon Composite Electrodes: Bulk-Modified Electrodes. Composite carbon–silicate electrodes (CCEs) were introduced by our group.[38] The ability to tailor integrated, multicomponent structures by sol–gel doping and ormosil formation are very well demonstrated in different electrochemical applications based on these composites.

Carbon–ceramic composite electrodes (CCEs) are comprised of a dispersion of carbon powder in organically modified or nonmodified silica matrixes. The electrodes are prepared by mixing appropriate amount of carbon black or graphite powder with the sol–gel precursors. A porous, brittle composite matrix is formed after gelation and drying. The composite electrodes benefit from the mechanical properties of the silicate backbone, from the electron percolation conductivity through the interconnected carbon powder and from the ability to manipulate the physicochemical characteristics of the matrix easily by incorporation of suitable monomer precursors or sol–gel dopants. CCEs enjoy the inherent versatility of the sol–gel molding technology. Thus, it is possible to cast silica–carbon matrixes in virtually any desired geometrical configuration, including flat layers spread on insulating or conductive matrixes, monolithic disks or rods and even in the form of miniature (approximately 20 μm in diameter) CCEs.[51,52]

Controlling the active section of CCEs: When hydrophilic silica forming monomers, such as TMOS or cyanoethyltrialkoxysilane are used as precursors, the resulting electrode is water permeable and its chemically modified variants can be used for large surface area applications such as reference electrodes and electrocatalytic applications.

When hydrophobic silica forming monomers, such as MTMOS are used the resulting electrodes reject water leaving only segregated islands of carbon at the outer surface in contact with the electrolyte. When 30 nm size carbon black powder (Ketjenblack 600EC, Akzo, Ltd) was used, the conductive area of the electrode in contact with the electrolyte was less than 1% of the geometric cross section area of the electrodes. This surface structure is often referred to as an ensemble of microelectrodes and it is favorable configuration for general-purpose working electrodes for dynamic applications and flow detectors (for example, in flow

Scheme 1. Catalyst-Modified Carbon−Ceramic Gas Electrode (after Ref 54)



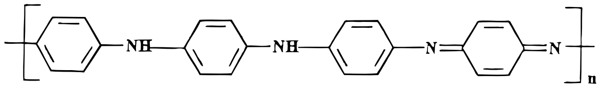
injection analysis or liquid chromatography). This configuration minimizes the background current that is proportional to the exposed conductive surface, while the sensing signal is determined by the diffusion of analyte to the geometric cross section of the electrode and therefore remains large. Indeed, the Faradaic signal to background current ratio was up to 3 orders of magnitude superior to the response of glassy carbon electrodes.[52] Incorporation of hydrophilic additives such as poly(ethylene glycol) or small amount of TMOS to the precursors of hydrophobic CCEs endows a degree of hydrophilicity and a controlled section of the electrode can be wetted by the electrolyte. The wetted section is very stable and remains constant even after several weeks in an electrolyte.[53,54]

Bulk-modified electrodes: Modified electrodes provide electrochemists with the ability to tailor electrode reactivity, which can be used to obtain highly sensitive and selective signals.[20] However, despite the enormous scientific activity, most of the electroanalytical applications of modified electrodes are at present used almost exclusively for scientific research and do not penetrate into standard laboratory practice, largely because reproducibility can be achieved only after careful surface pretreatment and poisoned or contaminated surface-modified electrodes have to be reconstructed each time from scratch. Bulk-modified, polishable electrodes such as carbon paste composite electrodes constitute an alternative approach. These electrodes are comprised of a mixture of carbon powder and viscous liquid such as Nujol or paraffin oil and can be bulk modified by incorporating suitable chemical modifiers in the oil or by adsorption on the carbon surface. However paste electrodes exhibit rather low in-use stability and the electrode has to be renewed frequently. Composite carbon−ceramic electrodes offer an alternative type of bulk modified, renewable and yet very stable electrodes.[51,54,55]

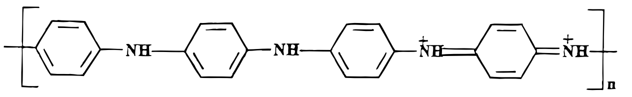
Graphite exhibits poor electrocatalytic activity but addition of trace metal or organometallic catalysts improves its performance. CCEs containing organometallic catalysts such as cobalt phthalocyanine and cobalt porphyrin showed pronounced electrocatalytic activity toward the reduction of O_2 and CO and oxidation of SO_2 and H_2.[54,55] High electrochemical sensitivity to hydrazine, hydrogen peroxide, oxalic acid, cysteine, and thiourea, which are important biomedical compounds, was recently demonstrated by Wang and co-workers.[56] Incorporation of the catalysts can be done by impregnation of the carbon powder with the organometallic catalysts prior to mixing with the sol−gel precursors or by adding the catalyst to the sol−gel precursors−carbon mixture, i.e., sol−gel doping. Inert metals (e.g., Pd, Au) can be also added in ionic form to the sol−gel precursors, and after electrode molding they can be reduced in situ by a flow of high-temperature hydrogen gas. Alternatively, preprepared inert-metal loaded graphite powders can also be used.[57,58]

Gas electrodes: Catalyst-modified CCEs can also function as gas electrodes. Gas electrodes are comprised of porous structure, permeable for gaseous compounds so that the gas feed can be introduced through the back side of the electrode, diffuse through it and react at the solid−liquid interface. Gas electrodes are finding numerous applications in fuel cells, batteries, electromachining, and gas sensing.[59] By far, the most successful example of these electrodes is the carbon−PTFE composite electrodes that were first introduced by Niedrach and Alford.[60] CCEs are potentially useful gas electrodes since their high porosity facilitates gas introduction through their backside (Scheme 1), and their hydrophobicity prevents flooding of the electrode by the electrolyte. Indeed, oxygen gas electrodes comprised of cobalt porphyrin and inert metal modified CCEs were reported by our group.[54,57,58]

2.3. Hybrid Interpenetrating Conducting Polymer−Metal Oxide Materials. Conductive π-conjugated polymers, such as the heterocyclic polymers (polypyrrole, polythiophene) and members of the polyaniline family (**8**) are important for their nonlinear optical (NLO) properties and as electrochemical materials. They are useful in diverse applications such as lithium intercalation batteries, capacitors, electrochromic displays, electrochemical signal mediators, and ion-selective field effect transistor sensors, ISFET.[61–63] Electrochemical polymerization of these materials provide a convenient way to deposit a controlled amount of the polymer on electrodes and also to encapsulate catalysts and biological species during the electrochemical polymerization process. Methods to improve the thermal and oxidative stability of these polymers and their adhesion to supporting metal transducers are required. Combining the favorable properties of inorganic gels and organic polymers can provide possible solution to some of the stability and adhesion problems. Rigid encapsulation by inorganic material can stabilize the organic polymers, and provide diffusion barrier against penetration of harmful oxidizers as well. Additionally, sol–gel films and silanized compounds[64] exhibit good adhesion to ITO (indium tin oxide) and other metal oxide coated electrode materials. The difficulties associated with the formation of thick (>1 μm) sol–gel films do not constitute an obstacle in this case due to the flexibility (and stress relaxation) entailed by the interpenetrating organic phase.



Emeraldine base (insulating form)



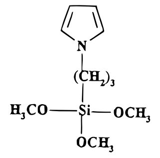
Emeraldine salt (conducting form)

8

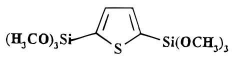
Interpenetrating organic–inorganic hybrids is a rapidly expanding research field in which sol–gel is playing a leading role,[32,65,66] thus it was natural that a number of creative sol–gel based synthesis procedures were developed for inorganic-conducting polymer hybrids.

(a) Sol–gel doping of preformed polymers: Here, a preformed polymer is first dissolved in an organic solvent, and the solution is then mixed with the sol–gel precursors. Inorganic sol–gel polymerization and subsequent solvent evaporation yield the desirable polymer-doped sol–gel matrix. Dunn and co-workers[67,68] used this method to prepare composite silicate–poly(ethylaniline) and polyaniline (in the insulating, emeraldine base state (**8**)). *N*-Methylpyrrolidinone was used to dissolve the polymer and then for homogenization of the water and silane precursors. The authors were interested in NLO and electric conductivity was not reported. A similar method was used by Wei and co-workers[69] to prepare polyaniline–polyacrylate–silica composites. The authors dissolved polyaniline and a copolymer made of 3-(trimethoxysilyl)propyl methacrylate and methyl methacrylate in *o*-cresol solvent and used this material for film casting. The authors report on a tradeoff between the electric resistivity of the film and its adhesion to the ITO support. Both increased when the ratio between the inorganic phase and the organic dopant was increased.

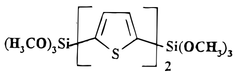
(b) Application of a silanized monomer for polymerization of both the π-conjugated polymer and the siloxane backbone: Sanchez et al.[70] used an alkoxide derivative of pyrrole (*N*-[3-(trimethoxysilyl)propyl]pyrrole (**9**)) as a common precursor for the sol–gel polycondensation and for organic polymerization of polypyrrole. Polymerization was conducted by chemical oxidation with ferric chloride. Electrochemical studies were carried out by incorporation of the gel into carbon paste electrode. The electrodes exhibited rather low stability and the electronic conductivity was also low 6×10^{-3} (S cm^{-1}). Corriu et al.[71] used a variant of this method to prepare polythiophene–silicates hybrids. Sol–gel polymerization of laboratory synthesized 2,5-bis(trimethoxysilyl)-mono-, bi-, and terthiophene (**10a–c**) formed thiophelene bridged silesquioxane gels (**11a–c**). The gel was deposited on a platinum electrode and thiophene was polymerized by repeated potential cycling. Splitting of the Si–C bond is a prerequisite to conjugation. Indeed cleavage of the Si–C bond coupled by anodic oxidation led to the production of polythiophene–ormosil. Similar conductive polymer–silicate networks were obtained by ferric chloride oxidation of the gel (**11**). The conductivity of the composites was not reported. Jang et al.[72] used a variant of this method to produce large-area electrochromic coatings. Polyaniline and polyacrylate–silica hybrid coatings were produced by introducing polyaniline into tetraethyl orthosilicate (TEOS) and poly[methyl methacrylate-*co*-3-(trimethoxysilyl)propyl methacrylate] sol–gel precursors. The silanized methacrylate precursor was prepared from 3-(trimethoxysilyl)propyl methacrylate (**12**) and methyl methacrylate with



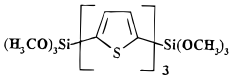
9



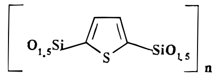
10a



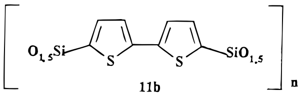
10b



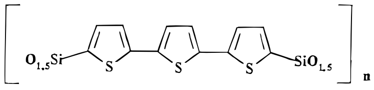
10c



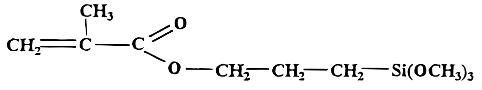
11a



11b



11c



$CH_2{=}C(CH_3){-}C({=}O){-}O{-}CH_2{-}CH_2{-}CH_2{-}Si(OCH_3)_3$

12

benzoyl peroxide initiator. Since several trialkoxysilane derivatives of aniline and pyrrole are commercially available, we believe that Sanchez' and Corriu's procedures will be optimized soon.

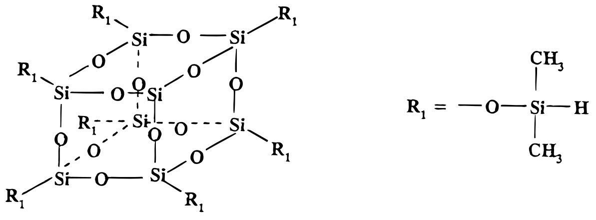
(c) Copolymerization of the sol–gel precursors and the organic monomers: Since conjugated polymers can be obtained electrochemically, it is possible to produce inorganic–organic interpenetrating copolymers by electrochemical polymerization in a solution phase containing sol–gel precursors with concurrent or subsequent inorganic polycondensation. Onoda et al.[73,74] synthesized polypyrrole–silicate films by electrochemical polymerization of pyrrole from dimethylformamide (DMF) solution containing TEOS and HCl catalyst. ITO-coated electrode was used as a substrate.

(d) Electrochemical polymerization of the conducting polymer in preprepared sol–gel film: Varghese and coworkers[75] introduced this approach for the production of polyaniline silicate composites. Aniline was electrochemically polymerized within the pores of a silicate film supported on a conductive substrate. However electric conductivity of these films were not reported or compared to native to pure electrochemically polymerized polyaniline coating.

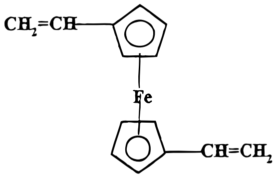
2.4. Redox Polymers. The term redox polymers is reserved to polymers in which the electron-transport mechanism is dominated by electron "hopping" between neighboring redox moieties. Movement of the reactive segments accompanies the charge transport. Additionally, the electron "hopping" or "self-exchange" is accompanied, under dynamic conditions, by diffusion of a counterion to preserve local electroneutrality. Therefore charge transport is usually described by an effective diffusion coefficient (D_{obs}) that is positively dependent on the concentration of the redox species in the polymer.[76]

Siloxane cross-linking is a popular way to obtain redox polymers or to attach redox functional groups onto metal oxides.[20,77,78] However, in the earlier studies on the preparation of redox films, less attention was devoted to the preparation and stabilization of the sols. Most of the recent studies still concentrate on modified siloxanes. To date the most efficient long-range charge-transfer films were developed by Wrighton and coworkers and Kepley and Bard starting with *N,N'*-bis-[-3-(trimethoxysylil)propyl-4,4'-bipyridinium] dichloride. The films were electroprecipitated from filtered basic sol (for homogeneity). Electrodeposition was conducted by repeated cycling of the potential between 0 and 0.78 V versus standard calomel reference electrode. These potential values correspond to the potential where the doubly charged monomer and the singly charged dimer are the dominant species, respectively. The authors focused attention on the electrochemical and elipsometric studies of the film rather than on the polymerization mechanism itself. Up to 5×10^{-8} mol/cm^2 and 500 nm thick films were deposited. The films exhibited rather large diffusion coefficient, $D_{obs} = 3 \times 10^{-9}$ cm^2/s. Interestingly, despite the highly cross-linked configuration, provided by the six hydrolyzable groups on the monomer, considerable reversible swelling (ca. 20%) was observed during oxidation/reduction of the film.

Moran et al.[79] studied the reaction of octakis(hydrodimethylsiloxy)octasilsesquioxane (**13**) with 1,1'-divinylferrocene (**14**) to give poly(ferrocenyloctasilsesquioxanes), a polymer that is comprised of three-dimensional octasiloxane units bonded by diethylferrocene bridges. This compound was deposited on a platinum electrode. Cyclic voltammetry indicated surface-confined redox couple and the integrated charge of the anodic and cathodic peaks were scan rate independent and corresponded to 3×10^{-9} mol/cm^2. This proves long-range transport by electron hopping mechanism since the redox species are immobilized and cannot diffuse to the electrode and the observed charge exceeds by far the expected charge for a monolayer.

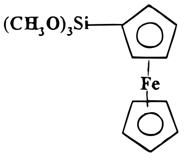


13

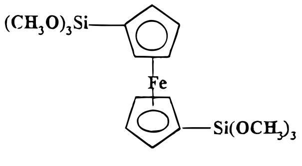


14

Audebert et al.[80,81] used (trimethoxysilyl)ferrocene (**15**) and 1,1'-bis(trimethoxysilyl)ferrocene (**16**) (preparation reported in ref 82) as sol–gel monomers. Copolymerization of **15** and **16** with TMOS yielded highly cross-linked, high surface area silica gels containing ferrocene groups. Cyclic voltammetry of deposited films made of **15** and TMOS deviated from the thin layer (surface-confined) behavior and showed apparent diffusion-limited pattern. The apparent diffusion coefficient, D_{obs}, varied in the range 10^{-9}–10^{-12} cm^2/s. D_{obs} was found to decrease with higher loading of ferrocene in the film. This deviation from the theoretical predictions was explained by changes in the specific surface area of the gels.

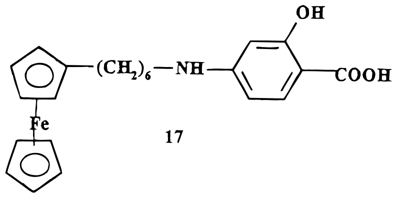


15

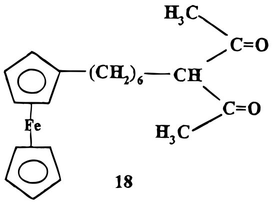


16

Audebert and Sanchez[34] reported recently a novel non-silicate organic–inorganic hybrid redox polymer. Zirconium alkoxides are highly reactive compounds that hydrolyze rapidly in water. However, a chelating agent such as acetylacetone replaces one of the alcohol ligands and forms a stable complex with the zirconium alkoxide. Audebert and Sanchez utilized this fact to attach ferrocenyl groups to sol–gel derived zirconium oxide. 4-[6-Amino-1-ferrocenylhexyl]salicylic acid (**17**) and 3-[6-1-ferrocenylhexyl]pentanedione (**18**) were used



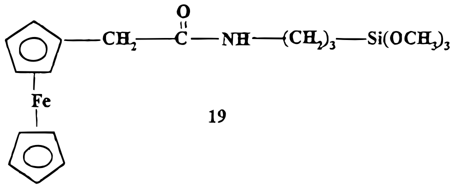
17



18

to chelate the zirconium alkoxide, which was hydrolyzed and condensed to form stable sols. The sols were deposited on platinum electrodes for electrochemical studies. CV showed diffusion-limited charge transport, and when the external section of the film was scratched off, a “thin-layer” electrochemical behavior was obtained. Studies of the apparent diffusion coefficient as a function of the ferrocene loading revealed positive dependence and good agreement with established theoretical predictions.

Our group introduced redox silicates, which were prepared by the copolymerization of *N*-[3-(trimethoxysilyl)propyl]ferrocenylacetamide (**19**) and MTMOS. The



19

material was used to prepare CCE-redox silicate electrodes.[83]

Polymer-coated electrodes are promising for diverse catalytic, sensing, and catalytic applications. However, studies of sol–gel derived redox-modified electrodes concentrated thus far only on the synthesis and electrochemical characterization of the films. With the exception of Bard’s work, very little was devoted to the structural and morphological characterization of the films and to studies on the dependence of the electrochemical characteristics of the modified electrodes on sol–gel processing parameters. Surprisingly, except for biosensing applications, which will be described separately, very little potential end applications were demonstrated so far.

3. Electrochemical Biosensors

In 1990 Braun and co-workers[84,85] encapsulated active enzymes in sol–gel silicates by mixing the biomolecules with the (methanol-poor) sol–gel precursors. Surprisingly, the enzymes withstood the harsh conditions of the inorganic polycondensation: they were not completely denatured by the alcohol solvent and remained active even after shrinkage of the porous structure during the drying stage. Ellerby et al.[86] first sonicated the alkoxysilane solution in order to prepare a silicate sol that contained little or no alcohol. The enzymes were then mixed with the sol in a conventional sol–gel procedure. In several cases the encapsulating enzyme were more stable than the native ones, presumably by formation of hydrogen bonds with surface silanols, which inhibit thermal reconformation.[87] A notable achievement was accomplished by Reetz and co-workers, by the encapsulation of lipases in hydrophobically modified silicates. Lipases are widely used for organic esterifications in hydrophobic media. The sol–gel-encapsulated lipases showed enhanced stability and reactivity as compared with the native ones[88,89] due to hydrophobic interaction with the Ormosil support. Sol–gel-encapsulated lipases are now marketed by Fluka.

More than 35 different types of hybrid biochemical–ceramic materials were tabulated in a recent review on sol–gel bioceramics.[90] Enzymes, antibodies, whole cells, whole cell extracts, and other active biological materials were encapsulated in a plethora of inorganic matrixes including silica, zirconia, and titania and composite titania–cellulose and silica–carbon matrixes.[91,92] Most of the activity is still directed toward the development of optical sensing, which benefits most from the transparency of silica and zirconia gels. However, recently sol–gel bioelectrochemistry attracts more attention since electrochemical biosensors can be used for on-line monitoring, while photometric biosensors are limited to batchwise, disposable devices. A prerequisite for an on-line electrochemical sensor is the ability to encapsulate active proteins in a thin active film. This is not simple: large concentration of alcohol and low pH conditions, which denature proteins are the favorable conditions for sol–gel film formation. Several synthetic pathways and sol–gel composites were employed to circumvent these problems, and those are briefly reviewed here.

Much of the electrochemical studies concentrated on glucose biosensing as a test case because of the stability of glucose oxidase and the medical importance of glucose sensing.[93] Glucose oxidase based electrochemical biosensors (and other oxidoreductase sensors) employ the following mechanism: D-glucose is oxidized to gluconolactone by reduction of a flavin group. The reduced flavin can then be reoxidized by oxygen, which is converted to hydrogen peroxide. Oxygen depletion or hydrogen peroxide anodic oxidation can be used for electrochemical quantitation of glucose. The enzyme regeneration step can also be carried out by a mobile redox couple, which can be electrochemically regenerated by an oxidation step on the electrode. By using this method, the signal is no longer dependent on the concentration of oxygen, and it is also possible to perform the detection/regeneration at lower voltages and thus decrease chemical interferences.

Silicate-Based Biosensors. Tatsu and co-workers[94] attached glucose oxidase doped silica powder to an oxygen electrode by a nylon membrane. Oxygen depletion was used to quantify glucose concentration. Audebert and Sanchez[95] developed a ferrocene-mediated biosensor by depositing glucose oxidase doped sol–gel film on an inert metal support. Ferrocenium was incorporated in the gel as an electron acceptor, and its reduction product ferrocene was continuously reoxidized on the electrode. 80% of the activity of the native glucose oxidase was retained in the gel. This technique was still limited to wet gels and once the xerogel was formed, the enzyme lost activity.

Narang et al.[96] immobilized glucose oxidase enzyme in a sandwich construction between two layers of sol–

gel derived silicate films deposited on an ITO substrate. Accumulated hydrogen peroxide was detected electrochemically. The signal of these electrode was however rather low, and the article focused on the optical aspects. Li et al.[97] applied horseradish peroxidase on carbon paste electrodes and deposited a TMOS-derived sol on top of this layer, and Yang et al.[98] prepared a miniature Pt-modified biosensor by coating Pt wire with glucose oxidase impregnated on preprepared sol–gel microspheres.

The sol–gel matrixes encapsulate very effectively the bulky enzymes and prevent their leaching to the solution; this however is not the case for many of the smaller mediators, which tend to leach from sol–gel membranes. Park et al. described a novel sol–gel-based procedure to prevent such leaching by coencapsulation of oxidoreductases (lactate oxidase, glucose oxidase) and redox polymer $[(Os)(bpy)_2(PVP)_{10}Cl]Cl$ (PVP stands for poly(4-vinylpyridine) in MTMOS-based sol–gel film.[99,100] Similar procedures were employed in the context of CCE biosensors which will be described below.

Non-silicate Biosensors. Several research groups reported biosensors based on non-silicate supports. Our group encapsulated glucose oxidase[101] and horseradish peroxidase[102] in vanadium pentoxide gel. V_2O_5 films exhibit reasonable electric conductivity due to doped V(IV) states, and they adhere well to conductive supports such as glassy carbon and platinum (particularly in the presence of the enzyme). Hydrogen peroxide oxidation was used for glucose quantitation.

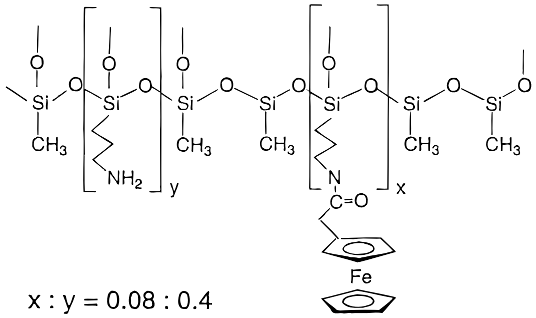
Milagres and co-workers[103] coated commercial silica gel by high surface area titanium dioxide layer using a modified sol–gel procedure and adsorbed ferrocene carboxylic acid and glucose oxidase onto the modified powder. Large loading of enzymes and mediators became possible due to the large surface area of the modified powder. The impregnated powders were incorporated in carbon paste electrode for electrochemical characterization.

Composite Carbon–Ceramic Biosensors. Another approach to shield the enzyme from the hostile environment during sol–gel synthesis is by first adsorbing it on a supporting platform that protects the enzyme from the environmental conditions. This method was used in the preparation of carbon–silica composite biosensors. Glucose oxidase doped CCE films could be formed at relatively high pH (pH 5–6) from methanol-free MTMOS-derived sol. Dissolved oxygen served as an electron acceptor, and the resulting hydrogen peroxide was electrooxidized on the electrode. Tetrathiafulvalene (TTF) and ferrocene-mediated glucose electrodes were also reported.[38,104] Slow leaching of the mediator was, however, observed during prolonged operation.

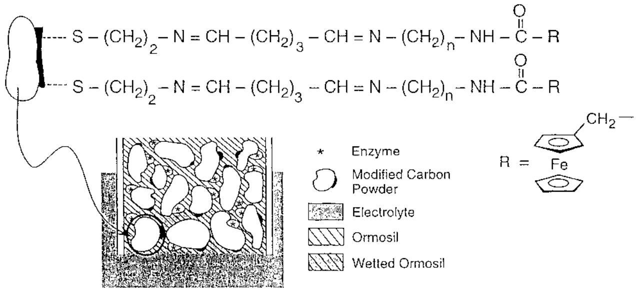
Three methods were used in order to prevent the leaching of mediators from the CCE biosensors.

1. *Encapsulation of mediator-modified enzymes in CCEs:*[105,106] In this construction, several ferrocene groups were covalently bonded to the glucose oxidase protein and then the protein was encapsulated in the sol–gel–graphite matrix. Thus, electron transfer from the active center of the enzyme to the carbon network was accomplished by a self-exchange mechanism, and leaching of the small mediator molecules was eliminated by their covalent bonding to the bulky entity.

Scheme 2. Structure of a Ferrocenyl-Modified Redox Silicate



Scheme 3. Structure of Ferrocene-Modified Carbon Particle



2. *Encapsulation of the oxidoreductase in redox-modified silicate–graphite composite electrodes:*[83,107] The electrode material was comprised of a dispersion of graphite powder and glucose oxidase incorporated in multifunctional, ferrocene-, amine-, and methyl-modified silicate polymer backbone (Scheme 2) prepared by the copolymerization of *N*-[3-(trimethoxysilyl)propyl]-ferrocenylacetamide (**19**), MTMOS, and aminopropylsilane. Each species in this integrated construction accomplishes a specialized task: the graphite powder provides conductivity by percolation; the silicate provides highly cross-linked and rigid backbone, which is used to cage the redox enzyme; ferrocene functional groups are responsible for the signal transduction from the active center of the enzyme to the electron conductive surface; the amine groups were incorporated for their high affinity to excess negative charges on the surface of glucose oxidase; finally, the combination of methyl and amine groups was advantageous to maintain control over the wetted electroactive section of the electrode.

3. *Immobilization of the oxidoreductase in silicate–redox-modified graphite powder composite electrode:*[108] This method is based on self-assembling the mediator onto the graphite powder. The carbon powder was first coated with gold and then derivatized stepwise with cystamine, glutaraldehyde, dialkylamine (e.g., 1,7-diaminoheptane), and finally with ferrocene acetic acid (Scheme 3). The modified graphite was then incorporated along with the enzyme in the sol–gel precursors. Cyclic voltammograms and steady-state tests revealed enhanced sensitivity for the longer spacers.

A way to decrease chemical interferences in amperometric determination of glucose is by using a dispersion of metal catalysts in the CCEs. The metallic catalysts lower the overpotential for hydrogen peroxide conversion and thus eliminate chemical interferences. Palladium-[53] and rhodium[109]-modified CCEs were developed by our group. Wang and co-workers[110] introduced ruthenium-dispersed sol–gel thick-film enzyme electrodes. In all cases[53,109,110] shelf-life stability of the electrodes exceeded 4 months. Both ruthenium oxide-[110] and rhodium[109]-modified electrodes exhibited remarkable selectivity for glucose over common medical interfering compounds, including ascorbic acid, acetaminophen, and uric acid. Electrodes for lactate (doped with lactate oxidase) and amino acids (amino acid oxidase) were prepared in a similar manner.[53] An interesting feature of the CCEs is that the active section of the electrode is not clogged upon repeated polishing due to the brittleness of the sol−gel silicate backbone, and thus the active section of the electrodes can be renewed by a mechanical polish after every use or contamination.

Recently, Coche-Guerente and co-workers[111] encapsulated both glucose oxidase and horseradish peroxidase in CCEs, thus devising a new type of mediatorless glucose sensor. Wang and co-workers[112] showed that sol−gel-derived hydrogen peroxide and glucose CCE test strips can be prepared by thick-film screen-printing technology (ink printing). This important accomplishment opens the door for mass production of disposable sol−gel-based CCE for biosensing and general sensing applications. This research also paves the way for micropatterning and production of electrode arrays by sol−gel processing. Sol−gel production of microdimension waveguides and waveguide sensors is rapidly developing due to the ability to control the viscosity of the sol and the gel time by judicial selection of pH, catalyst, and solvent. It is therefore to be expected that this capability will be rapidly exploited for the production of electrochemical multianalyte sensing electrodes.

4. Solid Electrolytes

Sol−gel processing of materials leading to ionically conductive glasses has been the subject of intense study and application-oriented development mainly in the areas of solid electrolytes and sensors. This is attributed to some of the properties of glassy materials such as wide composition flexibility, ease of fabrication, absence of grain boundaries, isotropic conduction, and high ionic coupled with low electronic conductivity.[113,114] In addition, the familiar advantages of sol−gel processing leading to large surface area materials and the ease of preparation of hydrated metal oxides also contributed to the proliferation of this area of research. This is especially true in the case of fast protonic conductors.[115−122] Ionic conductivity in these materials stems from the liquidlike motion of cations in the amorphous phase.[123,124] There have been several reviews[16,31,36,125−129] and symposia related to the sol−gel approach for the preparation of ionic conducting materials and studies involving solid electrolytes, sensors, and other applications. The main thrust of this area has been on protonic, sodium-, and lithium-based ionic conductors though other types of ionic conductors are periodically reported. In all these areas there are non-sol−gel-conductive materials that exhibit higher conductivity than the sol−gel ones, but the processibility of the sol−gel materials can provide an edge over other compounds, especially for thin-film applications. In this section, a detailed account of sol−gel-derived protonic conductors is followed by sodium and lithium ionic conductors. Subsequently, studies on other types of ionic conducting materials and sensors are briefly presented. The conductivity values given are at or close to ambient temperatures (≈25 °C), unless otherwise specified.

4.1. Protonic Conductors.

Fast protonic conductors are being developed with the final aim of using them in humidity sensors, hydrogen gas sensors, steam electrolyzers, and as electrolytes in electrochromic displays and solid electrolytes for hydrogen fuel cells. Optimum requirements for good protonic conduction include a high concentration of protons in the network in addition to the ionic mobility and chemical durability of the supporting glasses. This has imparted an edge in favor of sol−gel processing compared to conventional melt quenching processes which are carried out at >1000 °C that result in a low concentration of protons.

Silicates: The low mobility of protons in dry silica makes it a poor ionic conductor, and in fact the conductivity of xerogels is determined by the incorporated electrolyte rather than by the silicate backbone. However, the good processibility provided by sol−gel thin-film coatings and the very good account of the underlying science of thin-film formation have attracted considerable scientific interest to devise silicate-based protonic conductors. Conductive silicate-based materials were investigated in combination with imbibed electrolytes, with appropriate inorganic and organic dopants and with covalently linked aminosilane and other ormosils (the latter are called ormolytes and are discussed in the next section).

Dunn and co-workers[130] followed the conductivity of sol−gel-derived silicate gels during condensation and gelation. The proton conductivity of the initial silica sols and gels having a continuous aqueous solvent phase were reported to be comparable to that of aqueous solutions.

Heteropolyacids are known to have very high conductivity in the crystalline state. Hence, they are one of the best candidates for proton-conductive materials. However, thin-film casting of such materials is reported to be rather difficult.[121] Tatsumisago and co-workers[118,131] introduced heteropolyacid (dodecamolybdophosphoric acid, $H_3PMo_{12}O_{40}\cdot 29H_2O$, MPA) doped thin films. Humidity dependence on electrical conductivity revealed that there was almost 2 orders of increase in conductivity in the relative humidity range of 60−90%. A maximum conductivity of 3×10^{-3} S cm^{-1} was observed with a silicate film containing 42% MPA. The conductivity of the native MPA[127] was reported to be as high as 1.5×10^{-1} S cm^{-1}, which is 2 orders of magnitude superior to the conductivity of the encapsulated MPA. In another communication,[119] the same group demonstrated the usefulness of MPA-incorporated silicates as electrolytes in electrochromic devices.

Non-silicates: Amorphous phosphates were shown to be good proton conductors. Glassy zirconium phosphate was investigated as a protonic conductor[115,116] and conductivities of the order of 10^{-2} S cm^{-1} were achieved at room temperature. This material was found to be chemically stable, nonhygroscopic, and chemically stable at ambient conditions. Titanium phosphate based proton-conducting films with the composition 40 mol % TiO_2−60 mol % P_2O_5 were found to give reversible electrical resistance dependence on relative humidity.[132] The activation energy for proton transport in the film decreased with increase in relative humidity.

Forano and Besse[117] reported the preparation of antimonic acid, $HSbO_3\cdot nH_2O$, a material that shows fast protonic diffusion properties that makes it suitable for electrochromic and hydrogen detection devices. A maximum conductivity of 2.19×10^{-4} S cm^{-1} with an activation energy of 0.11−0.16 eV was reported. The application of this material was exemplified by demonstrating H_2 sensors and a Nernstian behavior was observed for the potential developed with the partial pressure of hydrogen. The potentiometric sensor for H_2 showed a response time of >60 s. The authors also demonstrated the amenability of this material for screen-printing technology.

Proton conduction in transition-metal oxide gels[36] such as $V_2O_5 \cdot nH_2O$ has been studied in detail since these are mixed electronic−ionic conductors with ionic part contributed from proton diffusion when the n value exceeds 0.5. The conductivity is related to the water molecules trapped in the layered V_2O_5 construction. Proton diffusion was found to occur through an ordered arrangement of water molecules and conductivities as high as 10^{-2} S cm^{-1} were observed. Ozer and Lampert[133,134] recently reported the preparation of Ta_2O_5 films on ITO substrates using $Ta(OC_2H_5)_5$ as the precursor. Proton conductivities of $>10^{-4}$ and 10^{-5} S cm^{-1} were observed using impedance measurements for amorphous and crystalline coatings, respectively.

Organic−Inorganic Materials. The hybrid organic−inorganic materials lead to modification or functionalization of the inorganic network that could be tailored for specific applications. Charbouillot and co-workers reported the preparation of hybrid materials wherein aminated organo silanes were used as the precursors.[136] The resulting transparent films called “aminosils”, exhibited proton conductivities of the order of 10^{-5} S cm^{-1}. Recently, a discussion was presented on the preparation of aminopolysiloxane gels by Zhmud and co-workers.[137] Another approach to tailor the organic−inorganic protonic polymer electrolytes was proposed by Gautier-Luneau and co-workers.[138] Their procedure involved (a) copolymerization of benzyltriethoxysilane with n-hexyltrimethoxysilane and organo-functional triethoxysilane followed by (b) sulfonation of the benzyl groups and (c) further cross-linking by hydrosilylation of the silane groups with divinylbenzene. The resulting poly(benzylsulfonic acid) siloxane had a conductivity of 10^{-2} S cm^{-1}, which is one of the highest reported for sol−gel-based ionic conductors. For comparison, the conductivity of Nafion,[127] which is considered to be one of the best and most used protonic conductor, is ca. 5×10^{-2} S cm^{-1} (activation energy = 0.22 eV). The silicate-based material showed good thermal stability up to ca. 250 °C, which makes it a promising solid electrolyte, e.g., for direct methanol/air fuel cells which operate at >100 °C. The proton conductivity of a rubbery material consisting of Ti−O−Ti network linked through organic bridges originating from glycerol and acetic acid, was found to be 10^{-5} S cm^{-1}.[135] The preparation procedure involved the hydrolysis of $Ti(OR)_4$ in the presence of glycerol and acetic acid. All the materials discussed thus far use organic modifiers in inorganic support; however, the inverse can also be accomplished. Nanocomposites comprised of mixed metal oxide (SiO_2-TiO_2 or $SiO_2-Al_2O_3$) and Nafion were prepared by sol−gel processing[139] and the structural topology were examined using various spectroscopic techniques, though conductivity values were not reported.

4.2. Sodium Ion Conductors. Fast ionic conductors based on sodium ions are one of the widest studied materials. Nasicon[140,141] has a general formula, $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ ($0 < x < 3$) and is very selective for sodium ions with a rather good conductivity that is higher than the aluminosilicate-based Na^+-selective membrane and β''-alumina. The maximum conductivity is observed when $x = 2$. The Nasicon framework is described as a rigid skeleton constituted by $(Si,P)O_4$ tetrahedra and ZrO_6 octahedra. The Na^+ ions occupy the interstices and move in the skeleton structure through narrow bottlenecks and hence the ionic conductivity is assumed to be three-dimensional.[140,141] Nasicon-based fast ionic conductors are potential candidates for sodium−sulfur batteries, electrochromic displays, and ion- and gas-specific electrodes.

The sol−gel method for the preparation of nasicon and related phases was reported in the early 1980s, some 5 years after their first introduction by Goodenugh et al., and it continues to attract attention.[11,142−150] The conventional ball-milling method of preparing nasicon phases using the constituent oxides and carbonates results in impurities and undesirable variability in the final compound. Chemical coprecipitation with the component salts also could not avoid the formation of segregated zirconia phase during the high-temperature treatment.[151] In this direction, sol−gel processing could lead to relatively pure single-phase materials, since low sintering temperatures (<1100 °C) are sufficient while the segregation of ZrO_2 phase takes place only around 1100 °C.

Nasicon-type materials have been prepared in both single and polycrystalline forms. Preparation of single crystals of various compositions in the system $Na_{1+x}Zr_2P_{3-x}Si_xO_{12}$ were reported.[152] Several synthesis procedures have been proposed for the preparation of homogeneous gels of uniform composition. These methods are usually based on the judicial choice of stabilizing ligands such as citrate or acetyl acetone that complex and stabilize the fast hydrolyzing component of the sol−gel precursors[153,154] resulting in the prevention of phase separation. Another vivid research area involves different methods of casting thin and thick films using different coating techniques such as dip coating,[155] spin coating,[156] and screen printing.[157]

Other families of nasicon-type sodium ion conductors were also proposed. Compounds such as $Na_5RESi_4O_{12}$, where RE is a rare-earth metal represented by $Na_5YSi_4O_{12}$ (NYS) and $Na_5GdSi_4O_{12}$ (NGS), were synthesized by Fakhar-Bourguiba and co-workers.[158] Silicon tetramethoxide or gadolinium (yttrium) nitrates were used as precursors. The structure of these compounds contains $Si_{12}O_{36}$ rings parallel to the basal plane of the hexagonal cell. These rings form rigid columns and the ionic conductivity arises due to the mobile Na between them. The σ values derived are of the order of 10^{-3} S cm^{-1} at temperatures close to 80 °C with an activation energy of ≈0.25 eV. Sodium zirconium silicate of the formula $Na_4Zr_2Si_3O_{12}$ was prepared by Saito and co-workers,[159] and the ionic conductivity was reported to be of the order of 10^{-3} S cm^{-1}. This was found to be enhanced by 1 order of magnitude with an unchanged activation energy at all temperatures, when a solid superacid, SO_4^{2-}/ZrO_2, was dispersed into the material. The increase in conductivity was ascribed to interfacial conduction.

Nasicon-Based Sensors. Several authors employed the Na ion conductivity of nasicon and related materials for the preparation of a variety of potentiometric sensors.[155,160−165] For example, Caneiro and co-workers[160] studied the characteristics of sol−gel-synthesized nasicon for the performance of sodium ion sensors. Electrochemical characterization was carried out by impedance measurements, and the ion sensors were fabricated in two different modes: (a) with a liquid internal reference, Ag/AgCl/NaCl 0.1 M, pH 8/nasicon; (b) a solid-state device with a polymer as an internal ionic bridge, Ag/Polymer ($AgI_z^{(z-1)-}$, Na^+,I^-)/nasicon. The detection limit was found to be 3×10^{-4} mol/L, which is slightly inferior to the commercially available aluminosilicate membranes (Tacussel, France) that yield a detection limit of 2×10^{-5} mol/L. The selectivity for the interference of alkali ions, however, was better for the nasicon membranes than the commercial ones. Stability studies in water were, however, quite qualitative. Huang and co-workers[155] constructed nasicon-based sodium ion sensors using thin films of nasicon on Si−SiO_2 substrates. Capacitance−voltage characteristics were used for the quantification of sodium ion concentration. Leonhard and co-workers[157] prepared thick films of nasicon by the screen-printing technique and used it for sodium ion sensing. The sensitivity was, however, found to be less than the sintered pellets, and it was attributed to lack of dense packing that resulted in a decrease in specific conductivity.

Nasicon-based sensors for gaseous analytes such as CO_2 and NO_x have also been reported.[161−165] The sensing element consists of a solid ionic conductor and a catalytic metal oxide/metal salt as an auxiliary phase. The auxiliary phase of these elements acts as a catalyst and the mixed potential developed as a result of the introduction of gaseous analyte is measured with respect to a reference electrode. A CO_2 sensor made with $(Li,Ba)CO_3$ sensing electrode and an air (Pt,air) reference electrode coupled with nasicon ionic conductor showed a Nernstian response with high sensitivities to CO_2 (300−5000 ppm) and a good stability.[161] Nitrogen oxides released from automobiles and combustion facilities are serious pollutants and need constant monitoring. The potentiometric sensors based on ionically conducting materials are attractive for this purpose especially since the sensors based on metal salts as an auxiliary phase (except the one using $NaNO_2$) are not inherently suited for the detection of NO. The sol−gel-based NO_x sensor device[162] consisted of metal oxide/nasicon along with a gold mesh sensing electrode and Pt reference electrode and was used in a flow mode. The emf response with various metal oxides as auxiliary phases was followed, and Cr_2O_3 and CuO were found to be the most stable phases. A Nernstian response of 53 mV/decade for NO and 94 mV/decade for NO_2 were observed with response time ranging between 1 and 3 min at low concentrations of 100 ppm.

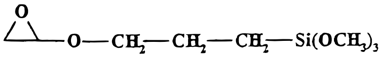
4.3. Lithium Ion Conductors. Lithium-based conductors have been the center of ionic conductivity research in the area of sol−gel processing for more than a decade. They have potential practical applications in solid electrolytes, especially as they are lightweight materials, leading to high energy densities that could pave the way to the reality of electric car. Generally, a lithium salt, LiCl or $LiNO_3$, is doped into the silicates during the preparation process. Sol−gel processing is quite useful in this direction since it leads to incorporation of high amounts of dopants during the film preparation stage with the possibility of tailoring large variations in the compositions.

Lithium chloride doped silicate gels follow the temperature−conductivity behavior typical of classical hopping mechanism, while the lithium nitrate doped gels do reveal a transition between low and high conductivity regions.[19] Similar findings were observed for their crystalline composite analogues. Klein, Greenblatt, and co-workers[166−175] and other researchers[176−183] have extensively studied this area and proposed methods based on sol−gel processing for the fabrication of thin films of electrolyte which would have smaller ohmic drops with prolonged life. Higher level of lithium (>30 mol %) could be achieved in the sol−gel films when a high water/TMOS ratio was used.[19] The long gelation time of 75 days allowed adequate control of viscosity of the sol and optimal film casting. The films were found to be very transparent having good adhesion to glass substrates. The preparation methods were found to have a bearing on the ionic conductivity of lithium silicate gels.[168] The hydrolysis of TEOS along with a lithium salt resulted in a better ionic conductivity (of the order of 10^{-2} and 10^{-5} S cm^{-1} at 400 °C for $LiNO_3$ and LiOH, respectively) than the soaking of previously formed colloidal silica gels in a solution containing lithium salt (10^{-4} and 10^{-6} S cm^{-1} at 400 °C for $LiNO_3$ and LiOH, respectively).

Other families of lithium-based ionic conductors include lithium aluminosilicates, lithium gallosilicates, and lithium borosilicates.[166,170,176−180] The conductivities of the members of these families are of the order of 10^{-4} S cm^{-1}. The conductivity, however, was found to vary with the ratio of B_2O_3 or Ga_2O_3 to SiO_2 in the matrix. This effect is attributed to increasing concentration of lithium ions associated with tetrahedral BO_4 or GaO_4 units and nonbridging oxygen atoms in the cell. Lithium aluminate-doped lithium orthosilicate showed only a marginal enhancement in the conductivity compared to pure lithium orthosilicate (10^{-4} S cm^{-1}). However, a heterogeneous material formed of a lithium silicoaluminate phase with Li_4SiO_4 type structure coexisting with lithium hydroxide showed higher values of 10^{-2} S cm^{-1}.[69,70] The electrical properties of highly oriented sol−gel prepared, lithium vanadium β bronze was investigated and ionic conductivity of the order of 10^{-1} S cm^{-1}at 350 °C was reported.[184] Ion conducting $LiNbO_3$ films were prepared by the sol−gel process using the metal ethoxides as precursors.[183] However, the conductivities were observed to be very low, 10^{-7} S cm^{-1}.

Compounds of the formula $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ that showed ionic conductivities of the order of 10^{-4} S cm^{-1} depending on the synthesis process were used as ionic membranes for lithium sensitive electrodes and the detection limit was found to be 1.4×10^{-4} mol/dm^{-3}.[185] These compounds also showed good stability in aqueous solutions.

Organic−Inorganic Materials. Organic−inorganic copolymers as hosts for lithium ions were synthesized[186] by the sol−gel process. It consists of an inorganic backbone (Si, Zr, etc.) chemically bonded to an organic network. Typically, 3-(methacryloxypropyl)trimethoxysilane (**12**) and 3-(glycidoxypropyl)trimethoxysilane (**20**)



20

were hydrolyzed, and on condensation ethylene glycol diglycidyl ether was added and polymerized at 60 °C. 1-Methylimidazole was used as a catalyst and an initiator for the copolymerization of the epoxy groups. Anhydrous lithium salts can easily be dissolved due to the presence of ion dissolving $(-OCH_2CH_2-)_n$ units. Dissolution of controlled amounts of $LiClO_4$ in the organically modified ceramic-containing grafted poly(ethylene oxide) leads to an amorphous electrolyte having ionic conductivities of 10^{-5} S cm^{-1} at room temperature and 10^{-3} S cm^{-1} at 125 °C.

Another class of ionic conductors called ormolytes (organically modified electrolytes) was recently introduced by Judeinstein and co-workers.[187,188] These are essentially transparent, composites containing TEOS, PEG (or PPG, polypropylene glycol), and $LiClO_4$. Several techniques such as IR, NMR, DSC, and SAXS showed that the material is diphasic containing fractallike SiO_2 clusters and PEG phase. The ionic conductivity was observed to be 10^{-4} S cm^{-1}. This is more than an order of magnitude better than the corresponding covalently linked organic–inorganic ormolytes. Presumably, polymer chain mobility contributes to the total conductivity of the PEG-doped silicate. Indeed the conductivity was increased when lower molecular weight PEG dopant was used and when the PEG content was increased.

4.4. Other Ionic Conductors. A new oxide ion conductor, $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}$, with a cubic perovskite structure was prepared by Huang and coworkers[189] from lanthanum, strontium, and magnesium acetates and gallium nitrate. Ac conductivities of the order of 0.11 S cm^{-1} at 800 °C were measured and these values are quite comparable to that of yttria-stabilized zirconia (≈0.1 S cm^{-1} at 1000 °C). This makes the sol–gel-derived materials good candidates for electrolytes in solid oxide fuel cells.

High-temperature sensing materials: Calcium β-alumina[190] was synthesized from alumina gel prepared from aluminum nitrate. β-Alumina powder made of sol–gel process[191] was shaped into desired configurations by three different methods, pressing, tape casting, and screen printing, and all three samples were found to be sensitive to CO_2 with high reproducibility. A new type of mixed potential sensor for CO using thick β-alumina films was recently proposed.[192,193] The sensor consisted of two metals with different catalytic properties (typically gold and platinum) deposited onto the two ends of a solid electrolyte pellet. The performance characteristics of the sensor was evaluated with a mixture of air and CO as the analyte, and a rather narrow dynamic range of 75–600 ppm was reported.

None of the sol–gel materials that were reviewed here show performance that is superior to the best materials obtained by other techniques. However, the versatility of sol–gel processing and particularly thin-film technology may provide an edge over other techniques. Inorganic–organic lithium and proton conductive composites were introduced only recently, but even at this stage their performance is equivalent to that obtained by the more mature technologies.

5. Sol–Gel Processing of Electrochromic Materials

Electrochromism (EC) is defined as a persistent and reversible change of color induced by electrochemical oxidation or reduction. The first description of electrochromism was presented by Kraus et al.[194] in a 1953 laboratory report describing that a vapor-deposited WO_3 layer was intensely blue colored upon cathodic polarization in sulfuric acid solutions. However, the technological significance of electrochromism was fully recognized only in 1969 by Deb;[195–197] then, worldwide research on electrochromism was initiated. Electrochromic materials are currently useful for smart windows, electronic displays, automotive rear and side view mirrors, and automotive sunroofs. Automotive mirrors have already been commercialized.[199,200] Thus the standing technological challenge in this field is to construct low-cost, large-area electrochromic devices.

An electrochromic device is comprised of several thin films. A typical five-layer device will have the following configuration: supporting glass/ITO/electrochromic anode or cathode/electrolyte/counter electrode/ITO/glass. The electrochromic material can be deposited either on the anode or on the cathode (e.g., WO_3) and the counter electrode should also provide charge storage (e.g., V_2O_5).[199] Solid or liquid electrolytes can be used as the separating electrolyte. It is clear that such multiple layer construction depends on reliable coating procedures, and today this can be realized mainly by vacuum techniques, i.e., sputtering and thermal vapor deposition or by sol–gel processing. The fact that sol–gel technology requires less expensive equipment for large-area coatings compared to vacuum techniques constitutes a much smaller advantage than anticipated on a first glance. First, the ITO coating is currently the dominant cost component, and the type of processing does not affect this. Additionally, the processing compatibility of the multilayered films constitute a technological challenge that is more demanding than the preparation and optimization of each film by itself. Electrochromic devices can be constructed by one of two ways: Subsequent deposition of all five layers on the same substrate, or starting with deposition of the anode and cathode materials on different ITO-coated glasses and subsequent lamination of the two coated glasses together by appropriate ion-conducting polymer. Retaining adhesion between five different deposited films or construction of homogeneous conductive polymer film that can adhere flawlessly and bind the coated glasses still present technological challenges. Methods to avoid release of volatile compounds during sol–gel film formation are needed for the practical realization of the lamination process.

Currently, there are two major types of electrochromic materials. Transition metal oxides or mixed oxides and organic electrochromic materials. The latter are based on electrochromic dyes (e.g., viologens) or conductive polymers such as the polyanilines. Additionally, there are interesting electrochromic materials such as the conducting polymer–vanadium oxide intercalates, which are still in a very preliminary stage of development. Sol–gel processing offers specific advantages in each of these categories.

5.1. Transition Metal Oxides. The electrochemical reaction in electrochromic transition metal oxides can be schematically represented as[194]

$$MO_n + xI^+ + xe^- \leftrightarrow I_xMO_n \tag{1}$$

where M is a metal, I^+ is a small monovalent cation such as H^+, Li^+, or Na^+, and n depends on the particular oxide. For example, n equals 2 for rutiles, $^3/_2$ for carborundums, and 1 for rock salts. The change in oxidation is accompanied by a change of ionic structure. For example, tungsten oxide goes from a distorted rhenium trioxide structure to a perovskite-like structure after electrochemical reduction, though luckily, in this case the change in structure is not accompanied by large volume change.[200]

Sol−gel processing of electrochromic devices is attractive for the following reasons: Sol−gel technology provides easy ways to control the microstructure of oxides. It provides techniques for the preparation of mixed oxides of controlled composition and homogeneity. The product of sol−gel processing is an amorphous hydrous gel, which is favorable as compared to the crystalline forms because of its better elasticity, which can accommodate volume changes caused by redox reactions and improved conductivity attributes. Sol−gel films adhere well to the transparent ITO or SnO_2 films. Finally, sol−gel processes can be carried out under ambient pressures, which provides an edge over the vacuum coating techniques especially for large-area devices.[198]

Thin electrochromic films can be deposited onto various substrates by spin- or dip-coating techniques, and brush or spray coatings are also possible for large area applications. The sol−gel precursors can be comprised of inorganic metal salts in aqueous solutions (e.g., tungsten oxide hydrate, $WO_3 \cdot nH_2O$ films prepared by the acidification of tungstate aqueous solution[207]) or metal in organic solvents (e.g., sol−gel-derived thin α-WO_3 films produced from tungsten hexaethoxide in butanol solution[221]). Chelating agents such as acetylacetonate can be used to control the rate of hydrolysis and oxolation and thus affect the porous structure. A final heat treatment can be used to control the microstructure, crystallinity, and pore size distribution of the films. The microstructure of the coatings can largely influence the kinetics, durability, color efficiency, and charge storage in the electrochromic electrodes. Electrochromic materials should exhibit good ionic conductivity and somewhat voluminous, low-density structure to provide rapid ionic mobility, though excess water will cause fast dissipation of the color. Amorphous materials are preferable in order to accommodate changes in structure without developing excess internal stresses and due to their improved ionic conductivity.

Several comprehensive reviews on transition-metal oxide electrochromic materials have recently been published.[197−206,257,258] A brief description of the most popular sol−gel electrochromic oxides follows, along with a comparison of their coloration efficiency (CE) with best values reported in a comprehensive review on vacuum-deposited electrochromic films.[200] CE is defined as the change of the optical density (ΔD) between the bleached and colored states divided by the injected charge (Q) per electrode cross section area. CE and ΔD are both wavelength-dependent parameters.[200]

Cathodically Colored Transition-Metal Oxide Materials. *Tungsten oxide:* Tungsten oxide is the first reported and still the best-performing transition-metal electrochromic material. The color of WO_3 changes from transparent or yellow to blue upon film reduction. The first published results for sol−gel derived electrochromic WO_3 film was by Livage et al. in 1984.[12] Since then, a large number of sol−gel preparation protocols were reported for pure WO_3[12,207−222] and for mixed oxides.[223−228] Typical CE values of sol−gel films were reported to be 70 cm^2/C (at 685 nm)[223] to 167 cm^2/C (at 800 nm)[222] as compared to 115 cm^2/C(at 633 nm) for amorphous films produced by thermal evaporation and 42 cm^2/C (at 650 nm) reported for sputtered polycrystalline films.[200] A specific benefit of sol−gel processing is the ability to produce mixed oxides of controlled composition. WO_3 shows low stability in aqueous systems, and thus titania−tungsten mixed oxides are often used.[223−228] The titania loading should be optimized to compromise between higher CE values and better stability, e.g., the CE of (1:3) TiO_2−WO_3 is lower by 50% as compared to pure tungsten oxides films.[223]

Titanium oxide: The color of TiO_2 films changes from transparent to either gray or blue upon reduction. Electrochromic TiO_2 coatings were prepared by diverse sol−gel protocols.[229−234] The CE of sol−gel-derived TiO_2 was reported to be 50 cm^2/C,[198] which is higher than the value reported for vacuum-deposited films (8 cm^2/C at 646 nm).[200]

Vanadium oxide: The coating color of V_2O_5 changes from red and yellow to green depending on the thickness of coatings. It possesses high ion-storage capability and high reversibility when used with lithium ions. Livage[17,235] recently reviewed the electrochemical and electrochromic properties of sol−gel-derived vanadium oxide. The electrochromic efficiency of the sol−gel-derived films are approximately 50 cm^2/C[198] as compared to $\approx$100 cm^2/C, which is characteristic of vacuum-deposited materials.[200] Vanadium oxide is often used as counter electrode in V_2O_5−WO_3 electrochromic devices.

Niobium oxide: Niobium oxide exhibits a color change from transparent to brownish gray or blue. Niobia has excellent chemical stability and corrosion resistance in both acid and base media, which makes it useful in a wide range of electrochromic devices. The first attempt to fabricate sol−gel Nb_2O_5 film was made by Lee and Crayston[242] using a sol made of a mixture of $NbCl_5$ dissolved in ethanol, but the electrochromic efficiency was rather low, 6 cm^2/C (800 nm). Sol−gel preparation protocols of Nb_2O_5 films are reported in refs 236−244. A typical CE value of 38 cm^2/C at 700 nm was reported by Ohtani et al.,[243] which is inferior to the CE of sputtered niobia films (100 cm^2/C).[200]

Anodically Colored Transition-Metal Oxides. *Nickel oxide:* Nickel oxide is a cheap electrochromic material with high electrochromic efficiency. Nickel oxide films become darker upon electrochemical oxidation. Sol−gel synthesis of nickel oxide have attracted considerable interest in recent years.[245−250] The electrochromic response and color stability depend strongly on the deposition route and heat-treatment conditions. Typical CE values were found to be ca. 35−40 cm^2/C[245,246] at 450 nm, which are similar to the CE values reported for vacuum-deposited films.[200]

Cobalt oxide: The color change of cobalt oxides is from pale yellow to dark brown. The CE of this material is in the range 20−27 cm^2/C for vacuum-deposited films.[252] Recent studies of cubic spinel Co_3O_4[251] and spinel-type Co:Al oxide and Co:Al:Si oxide films[252] show CE values of 25 and 22 cm^2/C, respectively.

Transition-Metal Oxides for Counter Electrodes. Several transparent ion-storage counter electrodes were used in electrochromic cells. V_2O_5-, SnO_2-, and CeO_2-

based electrodes are the widely studied compositions.

Tin oxides: SnO_2 films exhibit reversible lithium insertion and high optical transparency. Several sol–gel preparation protocols were reported.[253–256] Orel et al. demonstrated that the ion-storage capacity of SnO_2 films can be increased by decreasing the particle grain size. Sb and Mo dopants increase the conductivity.[255,256]

Cerium dioxide: CeO_2 films are colorless in both reduced and oxidized forms. These are therefore proposed as possible counter electrode materials for electrochromic devices. However, the response time of CeO_2 films is rather low. Baudry et al. and other groups[257–265] showed that mixed CeO_2–TiO_2 films have good optical transmission and improved response kinetics, contributed by ionic conductivity of amorphous TiO_2. Mo-doped CeO_2 supported on SiO_2 matrix was also reported to increase charge capacity.[266] Camino[257] and Deroo[258] reviewed sol–gel preparations of CeO_2–TiO_2 coatings and discussed the effect of nanocrystallinity on the electrochromic properties.

Heteropolyacid-doped silicates: These compounds[118,119,131] were mentioned in the previous section for their high proton conductivity. Tatsumisago et al.[119] used the same materials (MPA- and WPA-doped silicates) for electrochromic applications as well. The composite materials showed better electrochromic properties in the doped form as compared to their native state. Stangar et al.[225] incorporated WPA in titanium oxide gel and demonstrated improved electrochromism as compared to silica-supported WPA. MPA- and WPA-doped silicates are currently at a much earlier stage of research and development as compared to the transition-metal oxide electrochromic electrodes. However, these early reports open the door for further studies on the electrochromic characteristics of the large classes of HPAs that can be encapsulated in transparent silicates.

5.2. Hybrid Organic–Inorganic Electrochromic Materials. Two general classes of organic electrochromic materials are available: the first is based on dyes such as viologens or pyridine-containing compounds, and the second involves conductive polymers such as polyaniline, polythiophene, polypyrrole and their derivatives. In both cases change of color or bleaching is induced by electrochemical reactions. Organic electrochromic materials have several advantages over transition-metal oxides, including a larger selection of colors, rapid switching capability, and simpler handling and flexibility of organic polymers as compared to metal oxides. Drawbacks, however, include irreversible side reactions, short lifetime, poor UV stability, and in some cases, inferior adhesion to ITO supports was reported.[200]

Sol–gel processing provides facile ways to prepare organic–inorganic hybrids, which promise ways to overcome some of the inherent problems associated with organic dyes. The adhesion of silanized polymers to the substrates is often improved as compared to unmodified polymer.[64] Thus sol–gel processing of silica conducting polymer hybrids seems to be a good method to improve the adhesion properties to ITOs and other metal oxides. It is also possible that the thermal stability of caged dyes and polymers will be improved in inorganic matrixes. A dedicated study, aimed at quantifying the improved stability of a model chromophore, 2,4-dinitroaniline, in silicate film did not show any improvement of thermal or oxidative stability. However, one negative study does not necessarily teach failure of the general underlying approach.

Synthetic procedures for sol–gel preparation of inorganic-conducting polymer hybrids were discussed in the section 2.3 on modified electrodes. Most of these studies were for NLO (nonlinear optical) applications, and electrochromism was not discussed. Notable electrochromic studies of hybrid inorganic–organic include the following:

Jang et al.[72] have recently described a low-cost, large-area polyaniline and polyacrylate–silica hybrid electrochromic coatings by the sol–gel technique. A solution of polyaniline and poly[methyl methacrylate-*co*-3-(trimethoxysilane)propyl methacrylate] were spray- or brush-coated on transparent ITO substrates to form robust electrochromic coatings. The silane functional groups on the polyacrylate chain acted as coupling and cross-linking agents to improve surface adhesion and mechanical properties of the composite coating. These coatings showed reversible color changes from transparent to green, when polarized at potentials between −0.4 and +0.4 V vs Ag/AgCl in a 0.2 M $LiClO_4$ acetonitrile solution. It is shown that the cycle lifetimes of polyaniline films were improved by incorporating the polymer in the polyacrylate–silica matrix. A similar composite polyaniline–PMMA–silicate was reported by Okamoto et al.[268]

Hagfeld et al.[269] proposed encapsulation of viologen molecules in TiO_2 nanoparticales using sol–gel process. This composite material combined the large active area of nanosized titania particles with the good electrochromic properties of viologen. The electrochromic efficiency of this system was 85 cm^2/C. Another interesting class of electrochromic hybrid materials is the intercalated vanadium oxide-conducting polymers, described in section 6.2. Detailed electrochromic characterization of these materials has not yet been reported.

In conclusion, despite the fact that WO_3–V_2O_5 is still the most promising electrochromic device and it can be realized by sol–gel processing, new directions involving mixed oxides and organically doped materials exploit better the unique advantages of sol–gel processing.

6. Supercapacitors, Gas Sensors, and Other Emerging Applications of Conductive Gels

This section reviews several recent reports on promising new directions using conductive transition-metal oxide gels. All these applications can be realized only in gels; their crystalline counterparts would have shown a much inferior performance or would not materialize at all. Novel supercapacitors, hybrid electrochromic materials, and electrochemical gas sensors are described.

6.1. RuO_2 Supercapacitors. Electrochemical capacitors, also called supercapacitors, are energy-storage cells containing electrodes with very large capacitance.[270] The capacitance is contributed by a double-layer component and pseudocapacitance resulting from redox reactions of adatoms on the electrode surface. Supercapacitors are very useful for high power density applications. The pseudocapacitance and the double-layer capacitance are both proportional to the surface area of the electrode. Therefore, carbon and RuO_2, which have large specific surface area and high conductivity, are favorable electrode materials.

In recent publications,[18,271] Jow and co-workers reported a moderate-temperature sol−gel technique for the production of hydrous ruthenium dioxide gels ($RuO_2 \cdot xH_2O$) for supercapacitor applications. The material is amorphous and electrically conductive. Specific capacitance values of up to 720 F/g were measured, which is double the best reported capacitance of RuO_2 electrodes. The material owes its high specific capacitance to its hydrous gel nature. Indeed, when the preparation temperatures exceeded 175 °C, a crystalline phase was formed and the specific capacitance dropped rapidly. The authors believe that the bulk $RuO_2 \cdot xH_2O$ contribute to the redox reaction

$$RuO_2 + yH^+ + ye^- \rightleftharpoons RuO_{2-y}(OH)_y \qquad (0 < y < 2) \tag{2}$$

This explains the observations of the insensitivity of the specific capacitance to the specific surface area of the electrodes and also the exceedingly large experimental capacitances. The authors claim that in anhydrous RuO_2 reaction 2 is conducted only on the surface of the electrode. In contrast, in the sol−gel-derived hydrous form the bulk is more easily reduced (probably by facile intercalation) and thus larger Faradaic capacitances can be obtained. Since redox-induced intercalation phenomena are quite common in metal oxides, it is likely that this research will open new directions for sol−gel electrochemistry of other transition metal gels as well.

6.2. Intercalated Organic Compounds: Vanadium Oxide Hybrids. Vanadium pentoxide is an electrochemically interesting material due to its high redox potential, good electronic and ionic conductivity, and reversible lithium intercalation properties. It is useful as a lithium-intercalated cathode, and in its dry gel form it is useful for antistatic coatings and other nonelectrochemical applications. Sol−gel synthetic pathways and the chemistry of vanadium oxide gels were recently reviewed.[36] The material is comprised of self-aligned ribbonlike fibers. The individual ribbons are about 100 nm long, 10 nm wide, and 1 nm thick.[36] Ambient air gels have the approximate composition of $V_2O_5 \cdot 1.8H_2O$, and the water is intercalated between the layered structure. The electronic conductivity of vanadium oxides stems from a hopping mechanism between doped V(IV) and V(V) states. The ionic conductivity stems from its hydrous, acidic character. Vanadium pentoxide can be represented in the poly(vanadic acid) form as $H_xV_2O_5 \cdot nH_2O$ (x was found to be approximately 0.4 by potentiometric titration). Hydrated crystalline V_2O_5 was never reported,[36] and the crystalline form has poor electronic and ionic conductivities.

The layered structure of vanadium pentoxide gels has been exploited to intercalate many cation species (e.g., ferrocenium, cobaltocenium, and viologen) by a cation-exchange process,[272,273] and due to its high oxidative power it can intercalate irreversibly oxidizable species such as benzidine[36,274] yielding vanadium bronzes. Ruiz-Hitzky et al.[275,276] have intercalated poly(ethylene oxide) (PEO), a lithium conductor, in vanadium pentoxide gels, and our group has demonstrated the incorporation of active enzymes into the gels.[101,102] Kanatzidis et al.[37,277,278] have synthesized a variety of organic polymers in the interlamellar space between the layers by in situ intercalation and polymerization of the monomers of conducting polymers such as aniline, pyrrole and 2,2′-bithiophene. The conductivity of the composites are higher than V_2O_5 gels (typical value is 0.1 Ω cm^{-1} for polythiophene composite.[278,279] The composites combine the favorable features of each constituent, the electronic conductivity is increased and mechanical integrity is enhanced. Possible use as electrochromic materials was also described, though the practicality of this seems rather remote. All these materials can be realized only due to the flexible, amorphous nature of gels, which allow intercalation. In this context, vanadium aerogels were recently reported by Hirashima et al.[280,281] and by Dunn and co-workers.[282] These materials showed efficient lithium intercalation and should exhibit other interesting electrochemistry as well.

6.3. Vanadium Oxide: Gas Sensors. Recently, Cox and co-workers[283,284] introduced a new type of amperometric gas sensor that can operate in the hydrous gel phase without additional liquid phase. They used doped vanadium oxide gels coated on microelectrodes; a third reference electrode was also installed in gel. Ferroine and other redox species were shown to retain their aqueous CV response in the hydrous gel. Moreover, the response of this electrode was not sensitive to the hydration level at certain water-to-gel ratios. This pointed toward the possible exploitation of this phenomenon for gas sensing. The authors report the successful determination of gaseous ammonia by potentiometric and amperometric methods, using platinum working electrode modified with mixed-valent ruthenium oxide catalyst. The mechanism and products of the catalysis were not fully resolved, though ammonia oxidation is postulated. However, an important issue was clearly demonstrated even at this feasibility demonstration stage of the research: Amperometric gas sensing and catalyses are feasible in hydrous transition-metal gels that are not connected to a liquid electrolyte. This opens new directions for “gas electrochemistry” using hydrous gels under controlled humidity and temperature conditions.

7. Sol−Gel Coatings for Corrosion Protection

Most metals are thermodynamically unstable in air and in aqueous systems, and they owe their durability to the formation of passive metal oxides. The application of sol−gel-derived stable oxide films on metals is therefore an obvious extension of natural processes. Corrosion prevention technology utilizes the following three methods: (1) metal alloying with components that enriches the surface by a corrosion-resistant component during a corrosion process; (2) addition of aqueous inhibitors, which adsorb strongly on the metal and prevent the reaction with the oxidizer; (3) surface coatings. The last method can be used to manipulate both chemical and mechanical properties of metal surfaces.

Sol−gel technologies excel in the production of thin, scratch-resistant metal oxide coatings, and research is now being conducted on the development and characterization of sol−gel coatings for corrosion protection. Inorganic, single, or mixed oxide films and ormocer films have been developed. The films were tested for high-temperature gaseous oxidation and also for wet corrosion. A comprehensive review on the subject was recently published.[30]

7.1. Inorganic Protective Coatings. Films containing SiO_2,[285−293] TiO_2,[285] Al_2O_3,[294] ZrO_2,[286,295−298]

CeO_2,[299] and binary or mixed oxides containing $ZrO_2-Y_2O_3$,[300,301] $SiO_2-Al_2O_3$,[286,302,303] SiO_2-CeO_2,[304] and $B_2O_3-SiO_2$[285,305] were reported. In all these cases, the films were prepared by spin or dip coating from aged or sonicated sols, followed by a high-temperature densification process. Protective characteristics of the films were investigated by weight gain under aggressive high-temperature oxidation,[285−287,295,296,300,302,305] weight loss under corrosion in aggressive water solutions,[286,289−291,303] or by electrochemical voltammetry[286,289−291,296−298,303] and ac impedance spectroscopy.[286,288,298] The properties of the films prior to and after corrosion tests were investigated using X-ray diffraction and electron microscopy.

The following limitations and ways to circumvent them were found:

(a) Sol−gel films are porous and thus cannot prevent penetration of water and oxygen to the metal surface. High-temperature treatment was used to decrease the porosity and stabilize the films. In all the reported cases, where electrochemical measurements were conducted, the densification process was found to be only partial, and the film was still porous after the heat treatment.

(b) Sol−gel coatings often crack during drying and densification. Films produced from sonicated or aged sols were found to fracture less and they were preferred in most studies.

(c) The expansion coefficients of the metals and of protective films are incompatible, leading to film failure during temperature fluctuations. To tackle this problem, the densification process was conducted by a gradual elevation of temperature. Additionally, ZrO_2 exhibits a high thermal expansion coefficient, and it can be used for corrosion protection of metal parts under high-temperature conditions.

(d) It is difficult to obtain thick sol−gel coatings by spin- or dip-coating techniques. Thick oxide coatings could be prepared by multiple dip coating−drying procedures. However, thick oxides are unable to accommodate mechanical stresses caused by deformation or difference in temperature expansion coefficients.

Other inherent limitations including the brittleness of inorganic films and lack of flexibility, which prevented coating on edges, and complex structures could be resolved only by using ormosils. A general conclusion seems to be that optimization of the high-temperature densification treatment is the key to successful coating. Densification process at high temperatures in air is accompanied by diffusion processes that produce mixed oxide phases that can partially cure pores and defects in the sol−gel coating. As a result, a composite layer with properties intermediate between the parent and the coated oxides is produced.[300] This eliminates sharp boundaries at the metal/coating interface. However, thermal treatment can also lead to crystallization and film failure. For example, Atik and co-workers showed that high-temperature treatment of stainless steel can result in segregation of chromium oxides which cause film failure.[295,297] Thus, the high-temperature densification process should be optimized for each alloy.

7.2. Protective Ormosil Films. Wrighton and his group were the first to report the use of organically modified silicates for corrosion protection on of n-type semiconductive photoanodes. They used ferrocenyl containing precursors such as (1,1′-ferrocenediyl)dichlorosilane or 1,1′-bis(triethoxysilyl)ferrocene to prevent oxidation of the photoanodes (e.g., Ge and Si).[25−27] Despite the fact that the stability of the protective films were much inferior to current sol−gel technology-based films, they exemplified the possible incorporation of active corrosion-preventive organo-functional groups in corrosion-protective films by covalent linkage.

Organically modified silicates can circumvent some of the limitations of inorganic sol−gel processing without compromising their favorable optic characteristics. Thicker, more flexible hydrophobic ormocer films[307−312] can be prepared. The use of composite films containing inorganic components such as ZrO_2[309−311] or Al_2O_3[308] enables one to combine high mechanical hardness, scratch resistance, and transprency of the inorganic component with the flexibility and good adhesion of organic substances. Ormocers, containing organo-functional groups that provide additional protection were also synthesized. Izumi et al.[313] used fluorinated alkoxysilanes (such as $CF_3(CF_2)_n(CH_2)_2Si(OCH_3)_3$) along with conventional zirconia sol−gel precursors to increase the hydrophobicity of protective sol−gel films. Another example is the inhibition of copper corrosion by application of tetramethoxymercaptosiloxane (TMSPT). Here, sacrificial reaction of sulfur groups with oxygen was used in addition to surface blocking. The corrosion rate was measured by weight loss, ACIS, and CV techniques, which showed good initial corrosion protection (80% corrosion inhibition) that gradually deteriorated due to hydrolysis of the Cu−O−Si bonds.

However, temperature stability of ormocers is limited to <200−300 °C, and thus they have to compete with commercially available organic lacquers.

There are several areas where sol−gel coatings can be very effective:

(a) Protection of metals in optical systems that are subjected to aggressive environments: Morales and Duran demonstrated that protective SiO_2 coatings can successfully be applied on silver and aluminum coated mirrors (for solar collectors).[314] Comparison of the reflectance efficiencies of protected and unprotected mirrors showed improved durability of the SiO_2-protected mirrors. This study points toward a specific type of application where sol−gel protective films can be very successful, i.e., flat surfaces, relatively high cost (optical) parts that are subjected to high temperatures and where optical properties are vital.

(b) Protective coating of outdoor sculptures. A combination of epoxy-functionalized silane (3-(glycidoxypropyl)trimethoxysilane) (**20**) and diphenylsilanediole provided optimal, removable protective films on bronze sculptures.[315]

In both cases, the optical characteristics cannot be compromised, scratch-resistant coating is vital, and good corrosion protection is required.

8. Electrochemical Probing of the Sol to Gel to Xerogel Transitions

Electrochemical techniques were proven to be useful in probing transitions during sol−gel processing. The faradic current and the bulk conductivity are highly dependent on the mobility of charge carriers and thus on the viscosity of the electrolyte. This was used by several groups to trace structural and chemical changes that accompany the sol−gel process.

Zhang and Murray[316] introduced free redox probes (e.g., methylviologen) and reactive redox monomers (e.g., *N*,*N′*-bis[3-(trimethoxysilyl)propyl]-4,4′-bipyridinium dibromide) into the starting sol−gel solution and monitored the electrochemical response during the propagation of the polymerization. The cyclic voltammetry (CV) peak currents reflected changes in the mobility of the probes. The diffusion current of the free, unreactive mediator decreased monotonically while the redox-modified monomer was immobilized rather fast and the diffusion currents dropped abruptly. Audebert and co-workers[317,318] employed chronoamperometry and CV to study the diffusion coefficient of three different redox probes during the sol−gel process. A free ferrocenylmethanol; a sol−gel reactive monomer, dimethylferrocenylmethyl(8-trimethoxysilyl)octylammonium bromide; and a strong chelating agent ethyl 2-ferrocenyl-3-oxobutanoate were used to probe sol−gel preparation of silica and transition-metal oxide (titania and zirconia) gels at different pHs. The combination of free and reactive redox probes allow studies of the initial stages of the hydrolysis and condensation as well as changes in bulk viscosity at later stages.

Breiter, Dunn, and co-workers[319,320] introduced ac impedance spectroscopy for studies of the evolution of the sol−gel process and gel aging. Changes in bulk resistance of sol−gel mixtures that were prepared at different pH were investigated. The resistivity was only slightly changed during sol formation and gelation. pH dependence of the resistivity revealed that at $pH < 4$ and $pH > 7$ the conductivity was comparable to the corresponding aqueous solution but it was somewhat higher than the reference solution at $7 > pH > 4$. This was attributed to contribution of the negatively charged silanols on the surface of the silica colloids.

A striking observation in all the above-mentioned electrochemical probe studies[316−320] is that the macroscopic gel formation (at the gel point) had no effect on the microenvironment of the redox species (or charge carriers) and that connectivity of the gel voids was retained throughout the gelation process.

9. Electrochemical Synthesis of Sol−Gel Precursors

Electrochemistry is a powerful method for synthetic preparation of metal alkoxides, which can be used as sol−gel precursors. Metal alkoxides were prepared by anodic dissolution of metals in dry alcohols. Szillard was the first to report the formation of magnesium ethylate and lead and copper methylates from the corresponding metal anodes in the presence of sodium methylate or ethylate.[321] Later, the preparation of a large number of alkoxides was patented. The electrosynthesis of Ta, Ga, Zr, Ti, and Si ethoxides was patented by Monsanto,[322,323] and those of Fe, Co, Ni, Mn, Sb, and Cu alkoxides by Lehmkuhl et al.[324,325]

Detailed studies of the preparation of metal alkoxides from the III−V group element anodes were conducted by Russian research groups and reported in several patents[326−328] and articles.[329,330] The process involves long-time electrolysis (10−15 h) at high voltages (30 V) in alcohol solutions in the presence of suitable supporting electrolytes such as, $(Bu_4N)Br$, $(Bu_4N)BF_4$, and NaBr.[329−331] For example, dissolution of Ti anode in 2-propanol yields titanium isopropoxide with 87% current efficiency. Co, Ni, Fe, Ga, Sc, Y, Ge. Ti, Zr, Nb, and Ta alkoxides were produced with current efficiencies higher than 64%.[329−332]

The reaction mechanism of alkoxide formation from metal anodes was suggested by Lehmkuhl and co-workers.[331] The process is comprised of anodic dissolution of the metal and formation of the corresponding halogenide MX_n. The halogenide diffuses to the cathode where the MX_n species are reduced to $MX_n^{\bullet-}$ anion radical and undergo ligand exchange to give $M(OR)_n$.

This scheme was further elaborated by Shreider et al.[329,330] They suggested that the transfer of metals from the anode to the cathode proceeds not in the form of metal halide but in the form of alkoxohalides $M(OR)_mX_{n-m}$. This was confirmed by electrolysis using divided cells. Indeed, if the formed metal alkoxohalide has low solubility, the process is terminated at this stage.

The use of this synthesis procedure for Be, Zn, Sb, Bi and Al derivatives was unsuccessful. Sc and Y alkoxides are formed in high yields only on porous anodes; on polished electrodes the process is complicated by olefinic hydrocarbon formation.

The following conditions are also required for metal alkoxides electrosynthesis: The potential of the metal deposition has to be more negative than the potential of the metal−halogen bond reduction of the alkoxohalide. Thus, metal chlorides, which usually have more negative reduction potentials in organic solvents in comparison to bromides and iodides (by approximately 0.5 V[333]), can terminate the formation of alkoxohalogenides. So, bromide or iodide, but not chloride supporting electrolytes should be used. It was also concluded that the electrochemical synthesis of metal alkoxides can be used only for metals having standard potentials in the range 0.1−2 V (vs NHE).[329,330]

Yanovskaya et al.[334] introduced methoxyethanol as a useful solvent for electrochemical synthesis of metal alkoxides. In many cases this resulted in over 100% current efficiency which implies that simultaneous electrochemical dissolution and chemical oxidation took place. This solvent can also be used for the synthesis of two- or three-element-containing compounds. For example, zirconium−yttrium compounds can be prepared by anodic polarization of yttrium in zirconium isopropoxide in methoxyethanol solution with a current yield of about 200%:

$$Y + Zr(O\text{-}i\text{-}Pr) + CH_3OC_2H_4OH \rightarrow Zr_xY_yO_n(OC_2H_4OCH_3)_m + H_2 \quad (3)$$

Three mechanisms contribute to the dissolution process: (1) electrochemical dissolution; (2) chemical dissolution (by interaction of activated yttrium with methoxyethanol); (3) dissolution due to complex formation in the system $Y(OR)_3-Zr(OR)_4-ROH$.[334] Yanovskaya et al.[335] further used $Zr_xY_yO_n(OC_2H_4OCH_3)_m$ for the preparation of $ZrO_2{\cdot}Y_2O_3$ of 0.2−0.5 μm thick films. Dielectric characteristics of these films were superior to sputtered ones. This process allows the preparation of other mixed oxides such as $BaTiO_3$, $MgTiO_3$, $LiNbO_3$, and Na_xMoO_3.[334]

10. Concluding Remarks

Two new trends appear to be dominant in contemporary sol−gel electrochemistry. The first is the increased attention devoted to amorphous gels. Sol−gel is no longer considered as a mere road to crystalline materials, the gel itself becomes increasingly an end to itself due to its better processibility, improved diffusion rate, large ion-exchange capacity, and other application-specific chemical properties. This trend is apparent for example in electrochromic electrodes and ionic conductors, where amorphous materials provide better ionic mobility and in intercalated material applications such as V_2O_5-based sensors or RuO_2-based suercapacitors where superior elasticity of the gels can accommodate volume changes with minimal stress.

Another trend, which is perhaps connected to the first, is the fast proliferation of organic–inorganic hybrids in all fields of electrochemistry. Lithium and proton conductors, scratch-resistant corrosion-protection coatings, modified electrodes, and electrochromic devices based on organically modified sol–gel materials are developing rapidly. In this context, the rapid expansion of biochemical–inorganic hybrids is worth noticing, particularly since enzyme-doped sol–gel materials are already commercially available and can be incorporated in film or bulk-modified electrodes.

Sol–gel electrochemistry is rather young, and often researchers are still (justly) excited by the mere feasibility of realizing an application by sol–gel technologies. Thus, many of the exciting new directions are still based on a description of an application without detailed critical comparison with alternative technologies. Time will tell which of these new directions will survive.

Current scientific attention is still devoted to the processing of one material for one application at a time. However, we believe that in the future we shall see more integrated, multiple-layer, multitask sol–gel constructions. A first seed of this approach is the construction of an all-gel electrochromic device by Livage and coworkers.[336] The working and counter electrodes as well as the solid electrolyte were fabricated by sol–gel processing. In the future, we expect to see batteries and supercapacitors constructed by multiple sol–gel coatings. Later, we anticipate, integrated devices comprised of the electrochemical cell or sensor, and its power supply combined into one multiple-layer construction will emerge. This, we believe, is an inevitable consequence of the technological drive for miniaturization, the capabilities of sol–gel processing, and the recently acquired belief in the power of higher free energy materials that were prepared by low-temperature processing.

Acknowledgment. We thankfully acknowledge the financial help of the GBF-BMBF, Germany, and the Israel Ministry of Science.

References

(1) Iler, R. K. *The Chemistry of Silica*; Wiley: New York, 1979.
(2) Brinker, J.; Scherer, G. *Sol–Gel Science*; Academic Press: San Diego, 1989.
(3) Klein, L. C., Ed. *Sol–gel optics: processing and applications*; Kluwer Academic Publishers: Boston, 1994.
(4) Avnir, D.; Klein, L.; Levy, D.; Schubert, U.; Wojcik, A. B. Organo-Silica Sol–Gel Materials. In *The Chemistry of Organosilicon Compounds*; Apeloig, Y., Rappoport, Z., Eds.; Wiley & Sons: Chichester, Part 2, in press.
(5) Philipp, G.; Schmidt, H. *J. Non-Cryst. Solids* **1984**, *63*, 283.
(6) Schmidt, H.; Rinn, G.; Ness, R.; Sporn, D. In *Better Ceramics through Chemistry III*; Brinker, C. J., Clark, D. E., Ulrich, D. R., Eds.; *Mater. Res. Soc. Symp. Proc.* **1988**, 743.
(7) Avnir, D. *Acc. Chem. Res.* **1995**, *28*, 328.
(8) (a) Pekala, R. W.; Alviso, C. T.; Lu, X.; Gross, J.; Fricke, K. *J. Non-Cryst. Solids* **1995**, *188*, 34. (b) Pekala, R. W.; Kong, F. M. *Am. Ceram. Soc. Polym. Prepr.* **1989**, *30*, 221.
(9) Ebelmen, J. J. *Ann. Chim. Phys.* **1846**, *16*, 129.
(10) Ditte, A. *C. R. Acad. Sci. Paris* **1885**, *101*, 698.
(11) Quon, D. H. H.; Wheat, T. A.; Nesbitt, A. *Mater. Res. Bull.* **1980**, *15*, 1533.
(12) Chemseddine, A.; Henry, M.; Livage, J. *Rev. Chim. Miner.* **1984**, *21*, 487.
(13) Yoko, T.; Kamiya, K.; Sakka, S. *Denki Kagaku* **1986**, *54*, 284.
(14) Fujishima, A.; Honda, K. *Nature* **1971**, *238*, 37.
(15) Dislich, H. In *Sol–gel technology for thin films, fibers, preforms, electronics and specialty shapes*; Klein, L. C., Ed.; Noyes: Park Ridge, NJ, 1988; p 50.
(16) Dunn, B.; Farrington, G. C.; Katz, B. *Solid State Ionics* **1994**, *70–71*, 3.
(17) Livage, J. *Solid State Ionics* **1996**, *86–88*, 935.
(18) Zheng, J. P.; Cygan, P. J.; Jow, T. R. *J. Electrochem. Soc.* **1995**, *142*, 2699.
(19) Mouchon, E.; Klein, L. C.; Picard, V.; Greenblatt, M. *MRS Symp. Proc.* **1994**, *346*, 189.
(20) Murray, R. W. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1983; Vol. 13, p 191.
(21) Lenhard, J. R.; Murray, R. W. *J. Am. Chem. Soc.* **1978**, *100*, 7870.
(22) Lenhard, J. R.; Murray, R. W. *J. Electroanal. Chem.* **1977**, *78*, 195.
(23) Kuo, K.-n.; Moses, P. R.; Lenhard, J. R.; Green, D. C.; Murray, R. W. *Anal. Chem.* **1979**, *51*, 745.
(24) Murray, R. W. *Acc. Chem. Res* **1980**, *13*, 135.
(25) Wrighton, M. S.; Austin, R. G.; Bocarsly, A. B.; Bolts, J. M.; Haas, O.; Legg, K. D.; Nadjo, L.; Palazzotto, M. C. *J. Electroanal. Chem.* **1978**, *78*, 429.
(26) Bookbinder, D. C.; Wrighton, M. S. *J. Am. Chem. Soc.* **1980**, *102*, 5125.
(27) Bolts, J. M.; Wrighton, M. S. *J. Am. Chem. Soc.* **1978**, *100*, 5257.
(28) Philipp, G.; Schmidt, H. *J. Non-Cryst. Solids* **1984**, *63*, 283.
(29) Avnir, D.; Levy, D.; Reisfeld, R. *J. Phys. Chem.* **1984**, *88*, 5956.
(30) Guglielmi, M. *J. Sol-Gel Sci. Technol.* **1997**, *8*, 443.
(31) *Proton Conductors: Solids, Membranes and Gels–materials and devices*; Colomban, P., Ed.; Cambridge University Press: Cambridge, 1992.
(32) Mark, J. E. *Heterogen. Chem. Rev.* **1996**, *3*, 307 and references therein.
(33) Kapoor, R. N.; Mehrotra, R. C. *J. Am. Chem. Soc.* **1960**, *82*, 3495.
(34) Cattey, H.; Audebert, P.; Sanchez, C. *New J. Chem.* **1996**, *20*, 1023.
(35) Livage, J. *J. Sol-Gel Sci. Technol.* **1993**, *1*, 21.
(36) Livage, J. *Chem. Mater.* **1991**, *3*, 578.
(37) Kanatzidis, M. G.; Wu, C.-G. *J. Am. Chem. Soc.* **1989**, *111*, 4239.
(38) Tsionsky, M.; Gun, G.; Glezer, V.; Lev, O. *Anal. Chem.* **1994**, *66*, 1747.
(39) Keomany, D.; Petit, J.-P.; Deroo, D. *Sol. Energy Mater. Sol. Cells* **1995**, *36*, 397.
(40) Anderson, C.; Bard, A. J. *J. Phys. Chem.* **1995**, *99*, 9882.
(41) Dagan, G.; Sampath, S.; Lev, O. *Chem. Mater.* **1995**, *7*, 446.
(42) Dvorak, O.; De Armond, M. K. *J. Phys. Chem.* **1993**, *97*, 2646.
(43) Watson, J.; Zerda, T. W. *Appl. Spectrosc.* **1991**, *45*, 1360.
(44) Petit-Dominguez, M. D.; Shen, H.; Heineman, W. R.; Seliskar, C. J. *Anal. Chem.* **1997**, *69*, 703.
(45) Levy, D.; Iosefzon, B. K.; Gigozin, I.; Zamir, I.; Avnir, D.; Ottolenghi, M.; Lev, O. *Sep. Sci. Technol.* **1992**, *27*, 589.
(46) Hsueh, C. C.; Collinson, M. M. *J. Electroanal. Chem.* **1997**, *420*, 243.
(47) Coche-Guerente, L.; Cosnier, S.; Desprez, V.; Labbe, P.; Petridis, D. *J. Electroanal. Chem.* **1996**, *401*, 253.
(48) Kim, W.; Chung, S.; Park, S. B.; Lee, S. C.; Kim, C.; Sung, S. D. *Anal. Chem.* **1997**, *69*, 95.
(49) Kimura, K.; Sunagawa, T.; Yokoyama, M. *Chem. Lett.* **1995**, 967.
(50) Kimura, K.; Sunagawa, T.; Yokoyama, M. *Chem. Commun.* **1996**, 745.
(51) Gun, G.; Tsionsky, M.; Lev, O. *Anal. Chim. Acta* **1994**, *294*, 261.
(52) Gun, G.; Tsionsky, M.; Lev, O. In *Better Ceramics through Chemistry*; Sanchez, C., Mecartney, M. L., Brinker, C. J., Cheetham, A., Eds.; *Mater. Res. Soc., Symp. Proc.* **1994**, 1011.
(53) Sampath, S.; Lev, O. *Anal. Chem.* **1996**, *68*, 2015.
(54) Tsionsky, M.; Lev, O. *Anal. Chem.* **1995**, *67*, 2409.
(55) Tsionsky, M.; Lev, O. *J. Electrochem. Soc.* **1995**, *142*, 2154.
(56) Wang, J.; Pamidi, V. A. P.; Parrado, C.; Park, D. S.; Pingarron, J. *Electroanalysis*, in press.
(57) Gun, J.; Tsionsky, M.; Rabinovich, L.; Golan, Y.; Rubinstein, I.; Lev, O. *J. Electroanal. Chem.* **1995**, *395*, 57.
(58) Rabinovich, L.; Gun, J.; Tsionsky, M.; Lev, O. *J. Sol-Gel Sci. Technol.* **1997**, *8*, 1077.
(59) Chizmadzhev, Yu A.; Chirkov, Yu G. In *Comprehensive Treatise of Electrochemistry*; Yeager, E., Bockris, J. O'M., Conway, B. E., Sarangapani, S., Eds.; Plenum Press: New York, 1983; Vol. 6, p 317.
(60) Niedrach, L. W.; Alford, H. R. *J. Electrochem. Soc.* **1965**, *112*, 117.
(61) *Handbook of conducting polymers*; Skotheim, T. A., Ed.; Marcel Dekker Inc.: New York, 1986; Vols. 1, 2.

(62) MacDiarmid, A. G.; Maxfield, M. R. Organic Polymers as Electroactive Materials. In *Electrochemical Science and Technology of Polymers*; Limford, R. G., Ed.; Elsevier Applied Science: London, 1987; p 67.
(63) Scrosati, B. Polymer Electrodes. In *Solid State Electrochemistry*; Bruce, P. G., Ed.; Cambridge University Press: Cambridge, 1995; p 229.
(64) Habib, M. A.; Maheswari, S. *J. Electrochem. Soc.* **1991**, *138*, 1692.
(65) Komarneni, S. *J. Mater. Chem.* **1992**, *2*, 1219.
(66) Novak, B. M. *Adv. Mater.* **1993**, *5*, 422.
(67) Nishida, F.; Dunn, B.; Knobbe, E. T.; Fuqua, P. D.; Kaner, R. B.; Mattes, B. R. In *Better ceramics through chemistry*; Zelinski, B. J., Brinker, C. J., Eds.; *Mater. Res. Soc. Symp. Proc.* **1990**, *180*, 747.
(68) Mattes, B. R.; Knobbe, E. T.; Fuqua, P. D.; Nishida, F.; Chang, E.-W.; Pierce, B. M.; Dunn, B.; Kaner, R. B. *Synth. Met.* **1991**, *41*, 3183.
(69) Wei, Y.; Yeh, J.-M.; Jin, D.; Jia, X.; Wang, J. *Chem. Mater.* **1995**, *7*, 969.
(70) Sanchez, C.; Alonso, B.; Chpusot, F.; Ribot, F.; Audbert, P. *J. Sol-Gel Sci. Technol.* **1994**, *2*, 161.
(71) Corriu, R. J. P.; Moreau, J. J. E.; Thepot, P.; Chi Man, M. W.; Chorro, C.; Lere-Porte, J.-P.; Sauvajol, J.-L. *Chem. Mater.* **1994**, *6*, 640.
(72) Jang, G.-W.; Chen, C.-C.; Gumbs, R. W.; Wei, Y.; Yeh, J.-M. *J. Electrochem. Soc.* **1996**, *143*, 2591.
(73) Onoda, M.; Moritake, T.; Matsuda, T.; Nakayama, H. *Synth. Met.* **1995**, *71*, 2255.
(74) Onoda, M.; Matsuda, T.; Nakayama, H. *Jpn. J. Appl. Phys.* **1996**, *35*, 294.
(75) Verghese, M. M.; Ramanathan, K.; Ashraf, S. M.; Kamalasanan, M. N.; Malhotra, B. D. *Chem. Mater.* **1996**, *8*, 822.
(76) Blauch, D. N.; Saveant, J. M. *J. Am. Chem. Soc.* **1992**, *114*, 3323.
(77) Rubinstein, I. In *Applied Polymer Analysis and Characterization*; Mitchel, J., Ed.; Hanser: New York, 1991; p 323.
(78) Kepley, L. J.; Bard, A. J. *J. Electrochem. Soc.* **1995**, *142*, 4129. Bookbinder, D. C.; Wrighton, M. S. *J. Electrochem. Soc.* **1983**, *130*, 1080.
(79) Moran, M.; Casado, C. M.; Cuadrado, I.; Losada, J. *Organometallics* **1993**, *12*, 4327.
(80) Audbert, P.; Cerveau, G.; Corriu, R. J. P.; Costa, N. *J. Electroanal. Chem.* **1996**, *413*, 89.
(81) Audbert, P.; Calals, P.; Cerveau, G.; Corriu, R. J. P.; Costa, N. *J. Electroanal. Chem.* **1994**, *372*, 275.
(82) Cerveau, G.; Corriu, R. J. P.; Costa, N. J. *J. Non-Cryst. Solids* **1993**, *163*, 226.
(83) Gun, J.; Lev, O. *Anal. Chim. Acta* **1996**, *336*, 95.
(84) Braun, S.; Rappoport, S.; Zusman, R.; Avnir, D.; Ottolenghi, M. *Mater. Lett.* **1990**, *10*, 1.
(85) Braun, S.; Rappoport, S.; Zusman, R.; Shteltzer, S.; Drukman, S.; Avnir, D.; Ottolenghi, M. In *Biotechnology: Bridging Research and Applications*; Kamely, D., Chakrabarty, A., Kornguth, S. E., Eds.; Kluwer Academic Publishers: Amsterdam, 1991; p 205.
(86) Ellerby, L. M.; Nishida, C. R.; Nishida, F.; Yamanaka, S. A.; Dunn, B.; Valentine, J. S.; Zink, J. I. *Science* **1992**, *225*, 1113.
(87) Shtelzer, S.; Rappoport, D.; Avnir, D.; Ottolenghi, M.; Braun, S. *Appl. Biochem.* **1992**, *15*, 227.
(88) Reetz, M. T.; Zonta, A.; Simpelkamp, J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 301.
(89) Reetz, M. T.; Zonta, A.; Simpelkamp, J.; Rufinska, A.; Tesche, B. *J. Sol−Gel Sci. Technol.* **1996**, *7*, 35.
(90) Avnir, D.; Braun, S.; Lev, O.; Ottolenghi, M. *Chem. Mater.* **1994**, *6*, 1605.
(91) Dave, C.; Dunn, B.; Valentine, J. S.; Zink, J. I. *Anal. Chem.* **1994**, *66*, 1120A.
(92) Braun, S., Avnir, D., Eds. *J. Sol−Gel Sci. Technol.* **1996**, *7*, one-half the issue (Biochemical Aspects).
(93) Wilson, R.; Turner, A. P. F. *Biosensors Bioelectron.* **1992**, *7*, 165.
(94) Tatsu, Y.; Yamashita, K.; Yamaguchi, M.; Yamamura, S.; Yamamoto, H.; Yoshikawa, S. *Chem. Lett.* **1992**, 1619.
(95) Audebert, P.; Demaille, C.; Sanchez, C. *Chem. Mater.* **1993**, *5*, 911.
(96) Narang, U.; Prasad, P. N.; Bright, F. V.; Ramanathan, K.; Kumar, N. D.; Malhotra, B. D.; Kamalasanan, M. N.; Chandra, S. *Anal. Chem.* **1994**, *66*, 3139.
(97) Li, J.; Tan, S. N.; Ge, H. *Anal. Chim. Acta* **1996**, *335*, 137.
(98) Yang, Q.; Atanasov, P.; Wilkins, E.; Hughes, R. C. *Anal. Lett.* **1995**, *28*, 2439.
(99) Park, T. M.; Iwuoha, I.; Smyth, M. R.; MacCraith, B. D. *Anal. Commun.* **1996**, *33*, 271.
(100) Park, T. M.; Smyth, M. R.; Freaney, R.; McShane, A. *Talanta*, in press.
(101) Glezer, V.; Lev, O. *J. Am. Chem. Soc.* **1993**, *115*, 2533.
(102) Glezer, V.; Tsionsky, M.; Gun, J.; Lev, O. *Abstract of 44th ISE Meeting*; Berlin, Germany, Sept 1993, p 580.
(103) Milagres, B. G.; Kubota, L. T.; de Oliveira Neto, G. *Electroanalysis* **1996**, *8*, 489.
(104) Pankratov, I.; Lev, O. *J. Electroanal. Chem.* **1995**, *393*, 35.
(105) Sampath, S.; Pankratov, I.; Gun, J.; Lev, O. *J. Sol−Gel Sci. Technol.* **1996**, *7*, 123.
(106) Sampath, S.; Lev, O. *Electroanalysis* **1996**, *8*, 1112.
(107) Gun, J.; Lev, O. *Anal. Lett.* **1996**, *29*, 1933.
(108) Sampath, S.; Lev, O. *Adv. Mater.* **1997**, *9*, 410.
(109) Sampath, S.; Lev. O. *J. Electroanal. Chem.* **1997**, *426*, 13.
(110) Wang, J.; Parsad, V. A.; Park, D. S. *Electroanalysis* **1997**, *9*, 52.
(111) Coche-Guerente, L.; Cosnier, S.; Labbe, P. *Chem. Mater.* **1997**, *9*, 1348.
(112) Wang, J.; Pamidi, V. A.; Park, D. S. *Anal. Chem.* **1996**, *68*, 2705.
(113) Ravaine, D. *J. Non-Cryst. Solids* **1985**, *73*, 287. Minami, T. *J. Non-Cryst. Solids* **1987**, *95*, 107.
(114) Livage, J.; Barboux, P.; Nabavi, M.; Judeinstein, P. *Solid State Ionics, MRS Symp. Proc.* **1989**, *135*, 131.
(115) Abe, Y.; Li, G.; Nogami, M.; Kasuga, T.; Hench, L. L. *J. Electrochem. Soc.* **1996**, *143*(1), 144.
(116) Atik, M.; Pawlicka, A.; Aegerter, M. A. *J. Mater. Sci.* **1995**, *14*, 1486.
(117) Forano, C.; Besse, J. P. *Mater. Chem. Phys.* **1988**, *19*, 567.
(118) Tatsumisago, M.; Minami, T. *J. Am. Ceram. Soc.* **1989**, *72*(3), 484.
(119) Tatsumisago, M.; Kishida, K.; Minami, T. *Solid State Ionics, Diffusion Reactions* **1993**, *59*, 171.
(120) Eschenbaum, J.; Rosenberger, J.; Hempelmann, R.; Nagesgast, D.; Weidinger, A. *Solid State Ionics* **1995**, *77*, 222.
(121) Abe, Y.; Hosono, H.; Akita, O.; Hench, L. L. *J. Electrochem. Soc.* **1994**, *141*, L64.
(122) Tatsumisago, M.; Minami, T. *Nippon Kagaku Kaishi* **1987**, *63*, 1958.
(123) Boden, N.; Leng, S. A.; Ward, I. M. *Solid State Ionics* **1991**, *45*, 261.
(124) Gray, F. M. *Solid Polymer Electrolytes, Fundamentals and Technological Applications*; VCH: New York, 1991.
(125) Livage, J. *Solid State Ionics* **1992**, *50*, 307.
(126) Klein, L. C. *Solid State Ionics* **1989**, *32−33*, 639.
(127) Colomban, Ph.; Novak, A. *J. Mol. Struct.* **1988**, *177*, 277.
(128) Kreuer, K.-D. *Chem. Mater.* **1996**, *8*, 610; *Symposium D on Solid State Ionics*; MRS Meeting, *Proc. Mater. Sci. Eng.* **1989**, *B3*. Schottner, G.; Rose, K.; Schubert, U. In Vincenzini, P., Ed.; *Intelligent Materials and Systems;* Proc. Symp. 8th World Ceramic Congress and Forum on New Materials.
(129) Nazri, G.-A., Tarascon, J. M., Schreiber, M., Eds.; *MRS Proc.*, **1995**; *Symp. on Solid State Ionics IV*, 1994.
(130) Durakpasa, H.; Breiter, M. W.; Dunn, B. *Electrochim. Acta* **1993**, *38*, 371.
(131) Tatsumisago, M.; Sakai, Y.; Honjo, K.; Minami, T. *J. Ceram. Soc. Jpn.* **1995**, *103*(2), 189.
(132) Li, G.; Nogami, M.; Abe, Y. *Solid State Ionics, Diffusion Reactions* **1996**, *83*, 209.
(133) Ozer, N.; Lampert, C. M. *J. Sol−Gel Sci. Technol.* **1997**, *8*, 703.
(134) Ozer, N.; Lampert, C. M. *Proc. SPIE* **1995**, *2255*, 456.
(135) Judeinstein, P.; Livage, J.; Zarudiansky, A.; Rose, R. *Solid State Ionics* **1988**, *28−30*, 1722.
(136) Charbouillot, Y.; Ravaine, D.; Armand, M.; Poinsignon, C. *J. Non-Cryst. Solids* **1988**, *103*, 325.
(137) Zhmud, B. V.; Sonnefeld, J. *J. Non-Cryst. Solids* **1996**, *195*, 16.
(138) Gautier-Luneau, I.; Denoyelle, A.; Sanchez, J. Y.; Poinsignon, C. *Electrochim. Acta* **1992**, *37*, 1615.
(139) Shao, P. L.; Mauritz, K. A.; Moore, R. B. *Chem. Mater.* **1995**, *7*, 192.
(140) Goodenough, J. B.; Hong, H. Y. P.; Kafalos, J. A. *Mater. Res. Bull.* **1976**, *11*, 203.
(141) Hong, H. Y. P. *Mater. Res. Bull.* **1976**, *11*, 173.
(142) Gordon, R. S.; Miller, G. R.; McIntyre, B. J.; Beck, E. D.; Rasmussen, J. R. *Solid State Ionics* **1981**, *3−4*, 243.
(143) Boilot, J. P.; Colomban, Ph.; Blanchard, N. *Solid State Ionics* **1983**, *9−10*, 639.
(144) Engell, J.; Mortensen, S.; Moller, L. *Solid State Ionics* **1983**, *9−10*, 877.
(145) Colomban, Ph. *Ceram. Int.* **1989**, *15*, 23.
(146) Fabry, P.; Huang, Y. L.; Caneiro, A.; Patrat, G. *Sens. Act. B* **1992**, *6*, 299.
(147) Suda, S.; Iwaida, M.; Yamashita, K.; Umegaki, T. *Solid State Ionics Diffusion Reactions* **1994**, *69*, 101.
(148) Barj, M.; Perthuis, H.; Colomban, Ph. *Solid State Ionics* **1983**, *11*, 157.
(149) Bouquin, O.; Perthuis, H.; Colomban, Ph. *J. Mater. Sci. Lett.* **1985**, *4*, 956.
(150) Perthuis, H.; Colomban, Ph. *Mater..Res. Bull.* **1984**, *19*, 621.
(151) Bayard, M. L.; Barna, G. G. *J. Electroanal. Chem.* **1978**, *91*, 201.
(152) Boilot, J. P.; Columban, P.; Collin, G. *Solid State Ionics, Diffusion Reactions* **1988**, *28−30*, 403.
(153) Ahmed, A.; Glasgow, C.; Wheat, T. A. *Solid State Ionics* **1995**, *76*, 143.
(154) Choy, J. H.; Han, Y.-S.; Kim, Y.-H.; Suh, K.-S. *Jpn. J. Appl. Phys.* **1993**, *32*, 1154.
(155) Huang, Y. L.; Caneiro, A.; Attari, M.; Fabry, P. *Thin Solid Films* **1991**, *196*, 283.
(156) Shimizu, Y.; Michishita, S.; Murata, T. *Jpn. J. Appl. Phys., Part 2, Lett.* **1995**, *34*, L833.
(157) Leonhard, V.; Erdmann, H.; Ilgenstein, M.; Cammann, K.; Krause, J. *Sens. Act. B* **1994**, *18−19*, 329.

(158) Fakhar-Bourguiba, N.; Gharbi, N.; Smiri-Dogguy, L.; Boilot, J. P. *Mater. Res. Bull.* **1988**, *23*, 1185.
(159) Saito, Y.; Asai, T.; Nakamura, O.; Yamamoto, Y. *Solid State Ionics, Diffusion Reactions* **1989**, *35*(3−4), 241.
(160) Caneiro, A.; Fabry, P.; Khireddine, H.; Siebert, E. *Anal. Chem.* **1991**, *63*, 2550.
(161) Lee, D.-D.; Choi, S.-D.; Lee, K.-W. *Sens. Act. B* **1995**, *24−25*, 607.
(162) Shimizu, Y.; Maeda, K. *Chem. Lett.* **1996**, 117.
(163) Sadaoka, Y.; Sakai, Y.; Manabe, T. *Sens. Act.* **1993**, *B15*, 166.
(164) Leonhard, V.; Fischer, D.; Erdmann, H.; Ilgenstein, M.; Koeppen, H. *Sens. Act.* **1993**, *B14*, 530.
(165) Sadaoka, Y.; Sakai, Y.; Manabe, T. *J. Mater. Chem.* **1992**, *2*, 945.
(166) Wang, B.; Szu, S.; Tsai, M.; Greenblatt, M.; Klein, L. C. *Solid State Ionics* **1991**, *48*, 297.
(167) Tsai, M.; Szu, S. P.; Wang, B.; Greenblatt, M. *J. Non-Cryst. Solids* **1991**, *136*, 227.
(168) Szu, S. P.; Greenblatt, M.; Klein, L. C. *Solid State Ionics* **1991**, *46*, 291.
(169) Ogasawara, T.; Klein, L. C. *J. Sol−Gel Sci. Technol.* **1994**, *2*, 611. Hayri, E. A.; Greenblatt, M.; Tsai, M. T.; Tsai, P. P. *Solid State Ionics, Diffusion Reactions* **1990**, *37*, 233.
(170) Wang, B.; Szu, S.-P.; Greenblatt, M.; Klein, L. C. *Chem. Mater.* **1992**, *4*, 191.
(171) de Lambilly, H.; Klein, L. C. *J. Non-Cryst. Solids* **1988**, *102*, 269.
(172) Klein, L. C.; Ho, S. H.; Szu, S. P.; Greenblatt, M. In *Applications of Analytical Techniques for the Characterization of Materials*; Perry, D. L., Ed.; Plenum: New York, 1991; p 101.
(173) Szu, S. P.; Greenblatt, M.; Klein, L. C. *J. Non-Cryst. Solids* **1990**, *121*, 119.
(174) LeBars, N.; Klein, L. C. *J. Non-Cryst. Solids* **1990**, *122*, 291.
(175) Klein, L. C.; Wakamatsu, H.; Szu, S. P.; Greenblatt, M. *J. Non-Cryst. Solids* **1992**, *147/148*, 663.
(176) Tatsumisago, M.; Yoneda, K.; Machida, N.; Minami, T. *J. Non-Cryst. Solids* **1987**, *95/96*, 857.
(177) Villegas, M. A.; Fernandez Navarro, J. M. *J. Mater. Sci.* **1988**, *23*, 2464.
(178) Nogami. M.; Moriya, Y. *J. Non-Cryst. Solids* **1982**, *48*, 359.
(179) Kumar, B. *Mater. Res. Bull.* **1984**, *19*, 331.
(180) Wang, B.; Szu, S.; Greenblatt, M.; Klein, L. C. *Solid State Ionics, Diffusion Reactions* **1992**, *53−56*, 1214.
(181) Smaihi, M.; Petit, D.; Korb, J. P.; Boilot, J. P. *J. Solid State Chem.* **1991**, *94*, 260.
(182) Smaihi, M.; Petit, D.; Gourbilleau, F.; Chaput, F.; Boilot, J. P. *Solid State Ionics* **1991**, *48*, 213.
(183) Ozer, N.; Lampert, C. M. *Sol. Ener. Mater. Sol. Cells* **1995**, *39*, 367.
(184) Bae, S.-Y.; Miyama, M.; Yanagida, H. *J. Am. Ceram. Soc.* **1994**, *77*, 891.
(185) Cretin, M.; Fabry, P.; Abello, L. *J. Eur. Ceram. Soc.* **1995**, *15*, 1149.
(186) Popall, M.; Durand, H. *Electrochim. Acta* **1992**, *37*, 1593.
(187) Judeinstein, P.; Titman, J.; Stamm, M.; Schmidt, H. *Chem. Mater.* **1994**, *6*, 127.
(188) Dahmouche, K.; Atik, M.; Mello, N. C.; Bonagamba, T. J.; Panepucci, H.; Aegerter, M. A.; Judeinstein, P. *J. Sol−Gel Sci. Technol.* **1997**, *8*, 711.
(189) Huang, K.; Feng, M.; Goodenough, J. B. *J. Am. Ceram. Soc.* **1996**, *79*(4), 1100.
(190) Bucko, M. M.; Cichocinska, M. *J. Eur. Ceram. Soc.* **1996**, *16*, 79.
(191) Montanaro, L.; Negro, A.; Pijolat, C.; Lalauze, R. *Ann. Chim. [Sci. Mater.*] **1995**, *20*, 399.
(192) Lalauze, R.; Visconte, E.; Montanaro, L.; Pijolat, C. *Sens. Act.* B **1993**, *13−14*, 241.
(193) Colucci, G.; Negro, A.; Visconte, E.; Pijolat, C.; Lalauze, R. *Ceram. Inter.* **1990**, *6*, 225.
(194) Granqvist, C. G. *Sol. Energy Mater. Sol. Cells* **1994**, *32*, 369.
(195) Deb, S. K. *Appl. Opt. Suppl.* **1969**, *3*, 192.
(196) Deb, S. K. *Philos. Mag.* **1973**, *27*, 801.
(197) Deb, S. K. *Sol. Energy Mater. Sol. Cells* **1995**, *39*, 191.
(198) Lee, G. R.; Crayston, J. A. *Adv. Mater.* **1993**, *5*, 434.
(199) Agrawal, A.; Cronin, J. P.; Zhang, R. *Sol. Energy Mater. Sol. Cells* **1993**, *31*, 9.
(200) Bange, K.; Gambke, T. *Adv. Mater.* **1992**, *2*, 10.
(201) Jones, S. M.; Friberg, S. E. *J. Mater. Sci. Lett.* **1996**, *15*, 1172.
(202) *Optical Materials Technology for Energy Efficency and Solar Energy Concersion XIII*; SPIE: Bellingham, WA, 1994; Vol. 2255, most of the issue.
(203) *Sol−Gel Optics II*; SPIE: Bellingham, WA, 1992; Vol. 1758, most of the issue.
(204) Nabavi, M.; Doeuff, S.; Sanchez, C.; Livage, J. *Mater. Sci. Eng,* **1989**, *B3*, 203.
(205) Aegerter, M. A.; Avellaneda, C. R.; Pawlicka, A. G.; Atik, M. *J. Sol−Gel Sci. Technol.* **1997**, *8*, 689.
(206) Haas, H. E.; Golder, R. B. In *Larger Area Chromogenics: Materials and Devieces for Transmittance Control;* Lampert, C. M., Grangvist, C. G., Eds.; SPIE Optical Engineering: Bellingham, WA, 1990; p 170.
(207) Livage, J.; Guzman, G. *Solid State Ionics* **1996**, *84*, 205.
(208) Taylor, D. J.; Cronin, J. P.; Allaed, L. F., Jr.; Birnie III, D. P. *Chem. Mater.* **1996**, *8*, 1396.
(209) Baker, A. T.; Bosi, S. G.; Bell, J. M.; MacFarlane, D. R.; Monsma, B. G.; Skryabin, I.; Wang, J. *Sol. Energy Mater. Sol. Cells* **1995**, *39*, 133.
(210) Nishide, T.; Mizukami, F. *J. Mater. Sci. Lett.* **1996**, *15*, 1149.
(211) Cronin, J. P.; Tarco, D. J.; Tonazzi, J. C. L.; Agrawal, A.; Kennedy, S. R. *Sol. Energy Mater. Sol. Cells* **1993**, *29*, 371.
(212) MacDonald, K. A.; Bell, J. M.; Barcznska, J.; Voelkel, G. *Proc. SPIE* **1993**, *2017*, 95.
(213) Nonaka, K.; Takase, A.; Miyakawa, K. *J. Mater. Sci. Lett.* **1993**, *12*, 274.
(214) Bell, J. M.; Green, D. C.; Patterson, A.; Smith, G. B.; Macdonald, K. A.; Lee, K.; Kirkup, L.; Cullen, J. D.; West, B. O.; Spiccia, L.; Kenny, M. J.; Weilunski, L. S. *Proc. SPIE* **1991**, *1536*, 29.
(215) Lee, K. D. J. *Kor. Phys. Sci.* **1991**, *24*, 306.
(216) Livage, J. *Solid State Ionics* **1992**, *50*, 307.
(217) Oi, J.; Kishimoto, T.; Kudo, T. *J. Solid State Chem.* **1992**, *96*, 13.
(218) Judeinstein, P.; Livage, J. *Mater. Chem.* **1991**, *1*, 621.
(219) Itoh, K.; Okamoto, T.; Wakita, S.; Niikura, H.; Murabayashi, M. *Appl. Organomet. Chem.* **1991**, *5*, 295.
(220) Takase, A.; Miyakawa, K. *Jpn. J. Appl. Phys.* **1991**, *30*, Part 2, l1508.
(221) Unuma, H.; Tonooka, K.; Suzuki, Y.; Furusaki, T.; Kodaira, K.; Matsushita, T. *J. Mater. Sci. Lett.* **1986**, *5*, 1248.
(222) Ohtani, B.; Masuoka, M.; Atsumi, T.; Nishimoto, S.; Kagiya, N. *Chem. Express* **1988**, *3*, 319.
(223) Gottsche, J.; Hinsch, A.; Wittwer, V. *Sol. Energy Mater. Sol. Cells* **1993**, *31*, 415.
(224) Orel, B.; Stangar, U. L.; Hutchins, M. G.; Kalcher, K. *J. Non-Cryst. Solids* **1994**, *175*, 251.
(225) Stangar, U. L.; Orel, B.; Hutchins, M. G. *Proc. SPIE* **1994**, *2255*, 261.
(226) Stoch, J.; Klisch, M.; Babytch, I. *Bull. Pol. Acad. Sci. Chem.* **1995**, *43*, 173.
(227) Yoshino, T.; Baba, N.; Yasuda, K. *Nippon Kagaku Kaishi* **1988**, *9*, 1525.
(228) Doeuff, S.; Sanchez, S. *C. R. Acad. Sci. Ser. 2* **1989**, *309*, 351.
(229) Ozer, N. *Thin Solid Films* **1992**, *214*, 17.
(230) Ozer, N.; Tepehan, F.; Bozkurt, N. *Thin Solid Films* **1992**, *219*, 193.
(231) Ozer, N.; Chen, D. G.; Simmons, J. H. *Ceram. Trans. Glasses Electron. Appl.* **1991**, *20*, 253.
(232) Bell, J. M.; Barczynska, L.; Evans, L. A.; MacDonald, K. A.; Wang, J.; Green, D. C.; Smith, G. B. *Proc. SPIE* **1994**, *2255*, 324.
(233) Nabavi, M.; Sanchez, C.; Livage, J. *Eur. J. Solid State Inorg. Chem.* **1991**, *28*, 1173.
(234) Nabavi, M.; Doeuff, S.; Sanchez, C.; Livage, J. *Mater. Sci. Eng.* **1989**, *B3*, 203.
(235) Livage, J.; Guzman, G.; Beteilie, F. *J. Sol−Gel Sci. Technol.* **1997**, *8*, 857.
(236) Ozer, N.; Rubin, M. D.; Lampert, C. M. *Sol. Energy Mater. Sol. Cells* **1996**, *40*, 285.
(237) Pawlicka, A.; Atik, M.; Aegerter, M. A. *J. Mater. Sci. Lett.* **1995**, *14*, 1568.
(238) Ozer, N.; Chen, D.-G.; Lampert, C. M. *Thin Solid Films* **1996**, *277*, 162.
(239) Ozer, N.; Barreto, Y.; Bueyueklimanli, T.; Lampert, C. M. *Sol Energy Mater. Sol Cells* **1995**, *36*, 433.
(240) Ohtani, B.; Iwai, K.; Nishimoto, S.; Inui, T. *J. Electrochem. Soc.* **1994**, *141*, 2439.
(241) Faria, R. C.; Bulhoes, L. O. S. *J. Electrochem. Soc.* **1994**, *141*, L29.
(242) Lee, R. G.; Crayston, J. A. *Mater. Chem.* **1991**, *1*, 381.
(243) Ohtani, B.; Iwai, K.; Nishimoto, S.; Inui, T. *J. Electrochem. Soc.* **1994**, *141*, 2439.
(244) Rauh, R. D.; Cogan, S. F. *Solid State Ionics* **1988**, 1707.
(245) Surca, A.; Orel, B.; Pihlar, B.; Bukovec, P. *J. Electroanal. Chem.* **1996**, *408*, 83.
(246) Surca, A.; Orel, B. *J. Sol−Gel Sci. Technol.* **1997**, *8*, 743.
(247) Miki, T.; Yoshimura, K.; Tai, Y.; Tazawa, M.; Ping, J.; Tanemura, S. *Proc. SPIE* **1995**, *2531*, 135.
(248) Miki, T.; Yoshimura, K.; Tai, Y.; Tazawa, M.; Jin, P.; Tanemura, S. *The 3rd IUMRS International Conference on Advanced Materials*; Tokyo, Japan, 1993; p KP12.
(249) Foure, C.; Delmas, C.; Fouassier, M. *J. Power Sources* **1991**, *35*, 279.
(250) Lampert, C. M.; Caron-Popowich, R. *Proc. SPIE* **1989**, *1149*, 56.
(251) Svegl, F.; Orel, B.; Hutchins, M. G.; Kalcher, K. *J. Electrochem. Soc.* **1996**, *143*, 1532.
(252) Svegl, F.; Orel, B.; Bukovec, P.; Kalcher, K.; Hutchins, M. G. *J. Electroanal. Chem.* **1996**, *418*, 53.
(253) Olivi, P.; Pereira, E. C.; Longo, E.; Vareila, J. A. *J. Electrochem. Soc.* **1993**, *140*, 5, L81.
(254) Gulliver, E. A.; Garvey, J. W.; Wark, T. A.; Smith, M. J. H.; Datye, A. *J. Am. Ceram. Soc.* **1991**, *74*, 1091.
(255) Orel, B.; Stangar, U. L.; Kalcher, K. *J. Electrochem. Soc.* **1994**, *141*, L127.

(256) Orel, B.; Stangar, U. L.; Opara, U.; Gaberscek, M.; Kalcher, K. *J. Mater. Chem.* **1995**, *5*, 617.
(257) Camino, D.; Deroo, D.; Salardenne, J.; Treuil, N. *Sol. Energy Mater. Sol. Cells* **1995**, *39*, 349.
(258) Keomany, D.; Petit, J.-P.; Deroo, D. *Sol. Energy Mater. Sol. Cells* **1995**, *36*, 397.
(259) Keomani, D.; Poinsignon, C.; Deroo, D. *Sol. Energy Mater. Sol. Cells* **1994**, *33*, 429.
(260) Strangar, U. L.; Orel, B.; Gabec, I.; Ogorevc, B.; Kalcher, K. *Sol. Energy Mater. Sol. Cells* **1993**, *31*, 173.
(261) Macedo, M. A.; Dall'Antonia, L. H.; Valla, B.; Agerter, M. A. *J. Non- Cryst. Solid* **1992**, *147/148*, 792.
(262) Tonazzi, J. C. L.; Valla, B.; Macedo, M. A.; Baudry, P.; Aegerter, M. A.; Rodriguez, A. C. M.; Bulhoes, L. O. *Proc. SPIE* **1990**, *1328*, 375.
(263) Baudry, P.; Rodriguez, A. C. M.; Aegerter, M. A.; Bulhoes, L. O. *J. Non-Cryst. Solids* **1990**, *121*, 319.
(264) Brinker, C. J.; Scherer, G. W. In *Sol−Gel Science*; Academic Press: London, 1990; Chapter 4.
(265) Makishima, H.; Kubo, H.; Wada, K.; Kitami, Y.; Shimohira, T. *J. Am. Ceram Soc.* **1986**, *69*, C127.
(266) Stangar, U. L.; Opara, U.; Orel, B. *J. Sol-Gel Sci. Technol.* **1997**, *8*, 751.
(267) Schutte, C. L.; Williams, K. W.; Whitesides, G. M. *Polymer* **1993**, *34*, 2609.
(268) Okamoto, N.; Sezaki, N. *Transactions of the Institute of Electronics, Information and Communication Engineers C−II*; 1990, Vol. J73C−II, Iss: 6, p 365.
(269) Hagfeld, N.; Vlachopouls, N.; Gilbert, S.; Gratzel, M. *Proc. SPIE* **1994**, *2255*, 297.
(270) Raistrick, D. I. In *Electrochemistry in Electronics*; Noyes Publications: Park Ridge, NJ, 1995.
(271) Zheng, J. P.; Cygan, P. J.; Jow, T. R. *J. Electrochem. Soc.* **1995**, *142*, 2699.
(272) Aldebert, P.; Paul-Boncour, V. *Mater. Res. Bull.* **1983**, *18*, 1263.
(273) Nakato, T.; Kato, I.; Kuroda, K.; Kato, C. *J. Colloid Interface Sci.* **1989**, *133*, 447.
(274) Masbah, H.; Tinet, D.; Crespin, M.; Erre, R.; Van Damme, H. *J. Chem. Soc., Chem. Commun.* **1985**, 935.
(275) Aranda, A.; Casal, B.; Galvan, J. C.; Ruiz-Hitzky, E. In *Chemical Physics of Intercalation II*; Bernier, P., et al., Ed.; Plenum Press: New York, 1993; p 397.
(276) Ruiz-Hitzky, E.; Aranda, A.; Casal, B.; Galvan, J. C. *Adv. Mater.* **1995**, *7*, 180.
(277) Kanatzidis, M. G.; Wu, C.-G.; Marcy, H. O.; DeGroot, D. C.; Kannerwurf, C. R. *Chem. Mater.* **1990**, *2*, 222.
(278) Wu, C.-G.; Kanatzidis, M. G.; Marcy, H. O.; DeGroot, D. C.; Kannerwurf, C. R. *Polym. Mater. Sci. Eng.* **1989**, *61*, 969.
(279) Fuji, T.; Katagiri, N.; Kimura, O.; Kabata, R.; Kurosawa, Y.; Hyashi, Y.; Ichi, I.; Oshawa, T. *Synth. Met.* **1995**, *71*, 2225.
(280) Hirashima, H.; Sudoh, K. *J. Non-Cryst. Solids* **1992**, *145*, 51.
(281) Sudoh, K.; Hirashima, H. *J. Non-Cryst. Solids* **1992**, *147*, 386.
(282) Chaput, F.; Dunn, B.; Fuqua, P.; Salloux, K. *J. Non-Cryst. Solids* **1995**, *188*, 11.
(283) Cox, J. A.: Alber, K. S.; Tess, M. E.; Cummings, T. E.; Gorski, W. *J. Electroanal. Chem.* **1995**, *396*, 485.
(284) Cox, J. A.; Alber, K. S. *J. Electrochem. Soc.* **1996**, *143*, L126.
(285) Innocenzi, P. C.; Guglielmi, M.; Gobbin, M.; Colombo, P. *J. Eur. Ceram. Soc.* **1992**, *10*, 431.
(286) De Lima, N. P.; Atik, M.; Avaca, L. A.; Aegerter, M. A. *J. Sol-Gel Sci. Technol.* **1994**, *2*, 529.
(287) De Sanctis, O.; Gomez, L.; Pellegri, N.; Parodi, C.; Marajofsky, A.; Duran, A. *J. Non-Cryst. Solids* **1990**, *121*, 338.
(288) De Damborenea, J.; Pellegri, N.; Duran, A. *J. Sol-Gel Sci. Technol.* **1995**, *4*, 239.
(289) Atik, M.; De Lima, N. P.; Avaca, L. A.; Aegerter, M. A.; Zarzycki, J. *J. Mater. Sci. Lett.* **1994**, *13*, 1081.
(290) De Lima, N. P.; Fernandes, M. R.; Avaca, L. A.; Atik, M.; Aegerter, M. A. *Quim. Nova* **1994**, *17*, 308.
(291) Vasconcelos, W. L.; Leite, D. C., submitted.
(292) Kato, K. *J. Mater. Sci.* **1992**, *27*, 1445.
(293) Kato, K. *J. Mater. Sci.* **1993**, *28*, 4033.
(294) Leite, D. C.; Vasconcelos, W. L., submitted.
(295) Atik, M.; Zarzycki, J.; R'Kha, C. *J. Mater. Sci. Lett.* **1994**, *13*, 266−269.
(296) De Lima, N. P.; Atik, M.; Avaca, L. A.; Aegerter, M. A. *J. Sol−Gel Sci. Technol.* **1994**, *1*, 177.
(297) Atik, M.; R'Kha, C.; De Lima, N. P.; Avaca, L. A.; Aegerter, M. A.; Zarzycki, J. *J. Mater. Sci. Lett.* **1995**, *14*, 178.
(298) De Lima, N. P.; Avaca, L. A.; Atik, M.; Aegerter, M. A.; Rocha-Filho, R. C. *J. Braz. Chem. Soc.* **1995**, *6*, 33.
(299) Atkinson, A.; Guppy, R. M. *J. Mater. Sci.* **1991**, *26*, 3869.
(300) Shane, M.; Mecartney, M. L. *J. Mater. Sci.* **1990**, *25*, 1537.
(301) Kun'ichi, M.; Kunio, S.; Yong Wey, M. *J. Am. Ceram. Soc.* **1995**, *78*, 347.
(302) Di Giampaolo Conde, A. R.; Puerta, M.; Ruiz, H.; Lira Olivares, J. *J. Non-Cryst. Solids* **1992**, *147−148*, 467.
(303) Atik, M.; De Lima, N. P.; Aegerter, M. A.; Avaca, L. A. *J. Appl. Electrochem.* **1995**, *25*, 142.
(304) Nelson, R. L.; Ramsay, J. D. F.; Woodhead, J. L. *Thin Solid Films* **1981**, *81*, 329.
(305) Guglielmi, M.; Festa, D.; Innocenzi, P. C.; Colombo, P.; Gobbin, M. *J. Non-Cryst. Solids* **1992**, *147−148*, 474.
(306) Izumi, K.; Murakami, M.; Deguchi, T.; Morita, A.; Tohge, N.; Minami, T. *J. Am. Ceram. Soc.* **1989**, *72*(8), 1465.
(307) Izumi, K.; Tanaka, H.; Uchida, Y.; Tohge, N.; Minami, T. *J. Non-Cryst. Solids* **1992**, *147−148*, 483.
(308) Kasemann, R.; Schmidt, H. *New J. Chem.* **1994**, *18*, 117.
(309) Izumi, K.; Tanaka, H.; Murakami, M.; Deguchi, T.; Morita, A. *J. Non-Cryst. Solids* **1990**, *121*, 344.
(310) Sugama, T.; Carciello, N.; Miura, M. *Thin Solid Films* **1992**, *216*, 249.
(311) Attik, M.; Luna, F. P.; Messaddeq, S. H.; Aegerter, M. A. *J. Sol−Gel Sci. Technol.* **1997**, *8*, 517.
(312) Schmidt, H.; Wolter, H. *J. Non-Cryst. Solids* **1990**, *121*, 428.
(313) Beccaria, A. M.; Bertolotto, C. *Electrochim. Acta* **1997**, *42*, 1361.
(314) Morales, A.; Duran, A. *J. Sol−Gel Sci. Technol.* **1997**, *8*, 451.
(315) Pilz, M.; Romich, H. *J. Sol−Gel Sci. Technol.* **1997**, *8*, 1071.
(316) Zhang, Y.; Murray, R. W. *P. H. Conf. Abs.* Mar, Pittsburgh, American Chemical Society, 1991.
(317) Audbert, P.; Griesmar, P.; Sanchez, C. *J. Mater. Chem.* **1991**, *1*, 699.
(318) Audbert, P.; Griesmar, P.; Hapiot, P.; Sanchez, C. *J. Mater. Chem.* **1992**, *2*, 1293.
(319) Durakpasa, H.; Breiter, M. W.; Dunn, B. *Electrochim. Acta* **1993**, *38*, 371.
(320) Durakpasa, H.; Breiter, M. W.; Dunn, B. *J. Sol-Gel Sci. Technol.* **1994**, *2*, 251.
(321) Szillard, B. *Z. Elektrochem.* **1906**, *12*, 393.
(322) *Ger. Offen.* **1972**, No. 2,121,732; *Chem. Abstr.* **1972**, *77*, No. 4885e.
(323) *Fr. Addn.* **1972**, No. 2,091,229; *Chem. Abstr.* **1972**, *77*, No. 96297r.
(324) *Ger. Offen.* **1974**, No. 2,349,561; *Chem. Abstr.* **1974**, *81*, No. 20237h.
(325) *Can. Pat.* **1978**, No. 1,024,466; *Chem. Abstr.* **1978**, *88*, No. 160737r.
(326) *USSR Pat. SU* **1982**, No. 953,008; *Chem. Abstr.* **1982**, *97*, No. 225708q.
(327) *USSR Pat. SU* **1983**, No. 1,008,282; *Chem. Abstr.* **1983**, *97*, No. 206568y.
(328) *USSR Pat. SU* **1986**, No. 1,237,658; *Chem. Abstr.* **1986**, *105*, No. 171830m.
(329) Shreider, V. A.; Turevskaya, E. P.; Kozlova, N. I.; Turova, N. Ya. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1981**, 1667.
(330) Shreider, V. A.; Turevskaya, E. P.; Kozlova, N. I.; Turova, N. Ya. *Inorg. Chim. Acta* **1981**, *53*, L73.
(331) Lehmkuhl, H.; Eisenbach, M. *Liebigs Ann. Chem.* **1975**, 672.
(332) Kessler, V. G.; Turevskya, E. I.; Kucheiko, S. I.; Kozlova, N. I.; Turova, N. Ya.; Obvintseva, I. E.; Yanovskaya, M. I. *Mater. Res. Soc. Symp. Proc.* **1994**, *346*, 3.
(333) Gutmann, V.; Nedbalek, E. *Monatsh.* **1957**, *88*, 320.
(334) Yanovskaya, M. I.; Solov'eva, L. I.; Kovsman, E. P.; Obvintseva, I. E.; Vorotolov, K. A.; Turova, N. Ya. *Integrated Ferroelectr.* **1994**, *4*, 275.
(335) Vorotilov, K. A.; Yanovskaya, M. I.; Dorokhova, O. A. *Integrated Ferroelectr.* **1993**, *3*, 33.
(336) Livage, J. *Solid State Ionics* **1988**, *28−32*, 1722.

CM970367B