

Sol–Gel–Xerogel Evolution investigated by Electroactive Probes in Silica and Transition-metal Oxide Based Gels

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Electrochemical techniques, including chronoamperometry, have been used to explore the evolution of composition and structure of silica and transition-metal gels prepared by sol–gel processes. Electroactive probes have been either freely dissolved into the gels or attached to the polymeric and oligomeric species. Their diffusion kinetics have been analysed in relation to parameters such as the gelation catalyst, the gel aging and drying. The results confirm predictions made by other techniques and shed new light on the behaviour of such systems.

Keywords: Sol–gel; Xerogel; Diffusion; Chronoamperometry

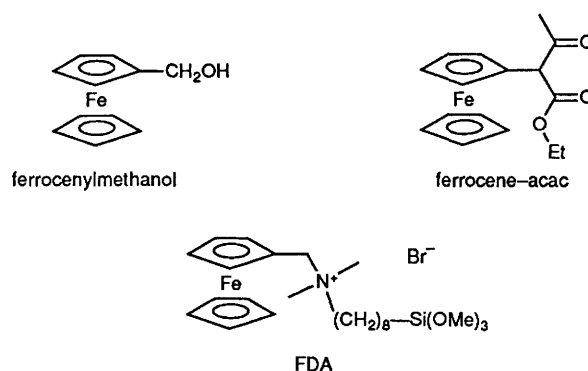
The synthesis of glasses and ceramics *via* sol–gel processes has received much scientific and technological interest during the last decade.¹ Sol–gel chemistry is mainly based on inorganic polymerization reactions.² Metal alkoxides [M(OR)_n; M = Si, Ti, Zr, ... where R is a 1- or 2-alkyl group] are used as molecular precursors for the sol–gel synthesis of metal oxides. These compounds are reactive species which lead to hydrolysis–condensation reactions when water is added. Metal oxide polymers are then obtained *via* these polymerization reactions.^{2b} Depending on the size and concentration of these inorganic oxy-polymers, sols and gels are formed. One of the main advantages of the sol–gel route is to allow a chemical control of the whole process, from the molecular precursor to the final material. Molecular precursors can be designed in the very early stages of the synthesis, thus providing opportunities to tailor the materials.^{2b}

A great amount of research is currently devoted to the characterization of the chemical species formed all the way from the molecular precursors up to the resulting materials.³ Many spectroscopic techniques are used: FTIR, multinuclear solid-state and liquid-state NMR, X-ray absorption (XANES and EXAFS). However, many physical properties of the resulting material such as porosity, mechanical integrity (dried coatings or bulk pieces without cracks and failures), transparency *etc.* are intimately related to the underlying polymer growth process and to the polymer texture in sols and gels upon aging and drying.

A detailed understanding of the underlying polymer growth process and of the evolution of the gel texture upon gelation, aging and drying is therefore essential and research is being carried out to study the physicochemical transformations that occur during the sol–gel–xerogel evolution. Fluorescence polarisation,⁴ two-dimensional NMR,⁴ rigidochromic fluorescent probes⁵ or non-linear optical probes⁶ have been used to characterize silicon oxide based gels. Recently, cyclic voltammetry studies have demonstrated the feasibility of electrochemical experiments in gelling systems.⁷ We recently reported how chronoamperometric measurements performed on ferrocene molecules embedded in gels can be a convenient method to access to the microviscosity of sol–gel systems.⁸ Such measurements do not necessarily require transparent matrices or deuteriated solvents.

This paper addresses a detailed and general description of the electrochemical behaviour of both silica gels and transition-metal oxide based gels loaded with various electroactive

compounds. The electroactive probes have been either simply embedded in the polymeric network or chemically anchored to the molecular precursors. A discussion on how the diffusion behaviour of these electrochemical probes can enlighten the microstructure of such systems is also included. We have mainly tested the behaviour of ferrocenic probes dissolved in gels made from aqueous alcohol. In our previous communication, simple unsubstituted ferrocene was used as the free probe, but in this work the choice was shifted towards ferrocenylmethanol (see Structure) which is far more soluble in aqueous alcohol. In this case any possibility for the electroactive probe to precipitate upon drying of the gel was avoided. We have also prepared ethyl 2-ferrocenyl-3-oxobutanoate, (designated Fc–acac), a ferrocene bearing an ethyl acetoacetate moiety which complexes strongly transition-metal ions such as Ti or Zr and therefore is attached to the polymeric skeleton, and dimethylferrocenylmethyl(8-trimethoxysilyl)octylammonium bromide (designated FDA), which is a ferrocene that can link itself to the polymeric skeleton during the polymerization step of a polysiloxane gel. These molecules are also given below. The electrochemical response of these different molecules introduced in silica or transition-metal oxide based gels is analysed and discussed.

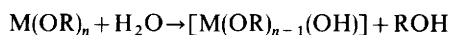


Experimental

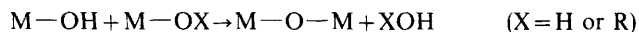
Molecular Engineering of Alkoxide Precursors

Sol–gel polymerization can be described as a two-step reaction.^{2a} Initiation is performed *via* the hydrolysis of alkoxy ligands. It leads to the formation of hydroxylated M–OH

groups:



Propagation then occurs *via* the polycondensation of these hydroxylated species giving rise to oxypolymers. Polycondensation implies an oxylation reaction which leads to the formation of oxygen bridges and the removal of XOH species as follow:



The chemical reactivity of metal alkoxides $M(OR)_n$ toward hydrolysis and condensation depends mainly on the electrophilicity of the metal atom and its ability to increase its coordination number.^{2a} Silicon alkoxide $Si(OR)_4$ precursors have a low electrophilicity and saturated coordination. Consequently their hydrolysis is slow and their polymerization reactions are mainly controlled *via* acid or base catalysis.^{1a}

The synthesis of monolithic polymeric gels needs a decrease in the functionality of the precursor towards hydrolysis together with a decoupling between hydrolysis and condensation rates. Condensation must be rather slow compared to hydrolysis. Acid catalysts are commonly used in silica gels to activate hydrolysis and to promote decoupling between the hydrolysis and condensation reactions. Transparent polymeric gels are thus obtained from acid-catalysed hydrolysis of $Si(OR)_4$.⁹ Activation of a silicon alkoxide precursor towards hydrolysis can also be performed by increasing the electrophilic character of the silicon atom. This has been performed by adding 4-dimethylaminopyridine (DMAP) which plays a double role as a base and as a nucleophilic catalyst. This process is named the SNASi¹⁰ mechanism.

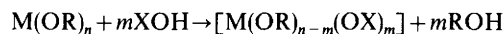
Preparation of Silica Based Gels

In a typical procedure,^{1a,7} tetramethoxysilane (TMOS) was dissolved in methanol containing the required amount of the electrolyte salt and the electrochemical probe. The ratio $F = \text{MeOH} : \text{TMOS}$ is found to be 6. The electroactive molecule concentration is adjusted to 0.01 mol dm^{-3} in the gel. Hydrolysis is then performed with a hydrolysis ratio $H_2O : Si = 7$. Different types of conditions have been used: DMAP, ($F = \text{DMAP} : Si = 0.003$), acidic catalyst (HCl) or without catalyst. At room temperature the DMAP catalysed gel is obtained within 9 min, in the other cases, gels are obtained within 24 h. The electroactive molecule (ferrocenylmethanol or FDA) is added by first mixing with TMOS. In the case of FDA-loaded gels, only acidic catalysis has been performed to allow this trifunctional alkoxide to bond the oxide network; the system has also been tested without catalysis. Into every sol-gel matrix, tetraethylammonium or tetrabutylammonium perchlorate (TEAP or TBAP) was added to make the gel conductive (TBAP and TEAP were found not to change the electrochemical behaviour of the gels). The concentration was adjusted to 0.1 mol dm^{-3} in the gel or 0.2 mol dm^{-3} in the special case of the experiments with ultramicroelectrodes.

Transition-metal Oxide Based Gels and Titanium Oxide Based Gels

Sol-gel chemistry of transition-metal alkoxides is more complicated.¹¹ Metal atoms have a high electrophilicity and they can exhibit several coordination states.¹² Molecular precursors are highly reactive so that the synthesis of transparent polymeric transition-metal oxide based sols and gels requires a careful control of the chemistry. Uncontrolled precipitation must be avoided. Therefore the first condition to fulfil is to perform an homogeneous generation of water. Water for hydrolysis of alkoxides can be diluted in a solvent or provided

in situ very slowly *via* a chemical reaction.¹³ The control of hydrolysis-condensation reactions is often performed *via* the chemical modification of metal alkoxides.¹⁴ Since transition-metal alkoxides are prone to nucleophilic reagents, they can be modified easily using complexing ligands HOX (OX = acetylacetonato, acetato) as follows:¹¹



Alkoxy groups (OR) are replaced by new ligands (OX) that can be less easily removed upon hydrolysis. Thus alkoxy ligands are first and rather quickly removed upon hydrolysis while chelating ones (the modifiers) act as termination agents, that inhibit condensation reactions.¹⁵

Titanium Oxide Based Gels

Typically ferrocene, ferrocenylmethanol or Fc-acac are added to $Ti(OEt)_4$ diluted in ethanol (ratio 1:2) (in the case of modification by Fc-acac, $Fc\text{-acac} : Ti = 0.05$). The hydrolysis was performed by adding water with hydrochloric acid (pH 0.7) diluted in ethanol (solution 10 wt.% in alcohol). The hydrolysis ratio is $F = H_2O : Ti = 2$. A gel is obtained within 10 min. The electroactive molecule concentration is adjusted to $10^{-2} \text{ mol dm}^{-3}$ in the gel in the case of a free probe and $3 \times 10^{-3} \text{ mol dm}^{-3}$ in the case of a linked probe.

Zirconium Oxide Based Gels

Zirconium oxide based gels¹⁶ were prepared by adding acetylacetone as a modifier (acetylacetone:Zr=0.4) to a solution of $Zr(OPr^n)_4$. The modified alkoxide is hydrolysed with a solution of water diluted in propanol (10% H_2O w/w in alcohol). The concentrations of the reagent were adjusted to yield a final mole ratio $Zr(OPr^n)_4 : PrOH : H_2O = 1 : 20 : 2$. Electrolyte (NET_4ClO_4) and probe concentrations were respectively 0.1 mol dm^{-3} , and 0.01 mol dm^{-3} . At room temperature a gel is obtained by $t_g = 30 \text{ min}$.

Synthesis of Probes

All compounds used for the preparation of the gels were commercial (Fluka) and were used without further purification. Water was distilled twice using a Millipore device. Ferrocenyl and ferrocenylmethanol were purchased (Aldrich). Fc-acac was prepared by a procedure adapted from Vogel.¹⁷ Ferrocenyl methanol is heated in an excess of ethyl acetoacetate in the presence of magnesium sulfate to remove water. Distillation of the excess of acetoacetate gives the C-alkylation product only¹⁸ which is further purified by flash chromatography (pentane:ether, 9:1). Mass spectra and NMR of the product confirm its structure (supplementary material available). FDA was simply obtained by quaternization of (ferrocenylmethyl) dimethylamine with the corresponding bromoalkylsiloxane in acetonitrile. The copper(II) dimethylphenanthroline perchlorate was simply prepared by reaction of stoichiometric amounts of copper(II) perchlorate and 2,8-dimethyl-1,10-phenanthroline.

Electrochemical Apparatus and Experiments

The liquid sol was poured into a cylindrical cell made of polystyrene (so that the gels do not attach to the walls of the container during drying), fitted with a tight cork in such a way that a small opening could be made. Within the cork Pt or glassy carbon working electrodes were sealed with an Ag wire as a quasi-reference and a platinum wire as a counter-electrode disposed in such a way that they were immersed in the gel (see Fig. 1). The size of the wires was minimized to

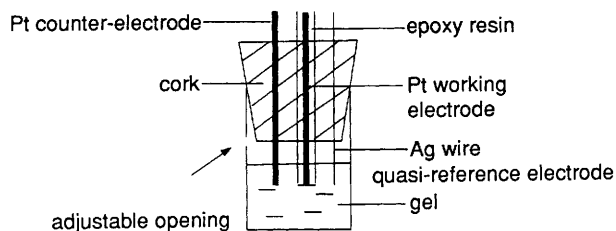


Fig. 1 Electrochemical cell used in sol-gel-xerogel experiments

avoid mechanical strain during the drying process, which could lead to the splitting of the partially dried gel. After the sol had been introduced, the cell was tightly closed until a time equal to $20\text{--}30t_g$ was reached (this time corresponds approximately to the time after which the gel ceases to change, as attested by the electrochemical response of the probe). A small opening was then made at the top of the cell so that the gel could be allowed to dry slowly and continuously over several days. The loss in mass of the gel was determined in a separate set of experiments by weighing a test sample at different drying stages and the shrinkage in volume estimated by measuring the dimensions of the test sample with a graduated instrument. The chronoamperometry is a current-potential method. Potential steps were applied at a potential $\geq +200$ mV above the redox potential of the probe so that Cottrell behaviour could be obtained, *i.e.* $i = FAC^\circ (\pi t)^{1/2}$ (where F = Faraday constant, A = electrode surface and C° = probe concentration) for a one-electron transfer. Hence, any influence of the electron-transfer kinetics on the probe could be avoided.

For slow chronoamperograms ($t = 10^{-3}\text{--}1$ s) and voltammograms ($V < 1000$ V s^{-1}), electrochemical instrumentation consisted of a PAR Model 175 Universal programmer and of homemade potentiostat equipped with a positive feedback compensation device.¹⁹ The data were acquired with 310 Nicolet oscilloscope.

In the case where microelectrodes were used, the ultramicroelectrode was a gold wire (5 or 17 μm diameter) sealed in soft glass.²⁰ The signal generator was a Hewlett Packard 3314A and the curves were recorded with a 450 Nicolet oscilloscope with a minimum acquisition time of 5 ns per point. The potentiostat was as previously published, without compensation for the ohmic drop.²¹

Results and Discussion

It is well known that three well defined states take place in the sol-gel-xerogel process. In the first phase, as soon as the hydrolysis begins, condensation reactions led to oligomers whose average weight increases steadily, this being evidenced by the increases of the macroscopic viscosity of the liquid, up to an infinite value which characterizes the gel point (time t_g). At this point a gel is formed, which appears macroscopically solid but is in fact formed of an extremely distended network, with large domains existing in solution and solvated oligomers unconnected to the percolating network of the gel. During the subsequent phase, which runs for a period of several t_g , this gel evolves, the 'free' oligomers progressively attaching to the main polymeric network. In the third period, the drying of the solvent allows the gel to harden and compact, creating a state in which no more free solvent molecules remain, which is called xerogel.

In such systems, electrochemical techniques, and more especially chronoamperometry, can give access to the kinetics of diffusion of the molecules that are contained inside the gels. If the molecules are free, that is, unconnected to large polymers, it can be assumed that they diffuse freely in the

liquid part of the gel which gives access to the microviscosity of their environment, as was shown in our previous communication.⁸ The microviscosity η (Fig. 2) experienced by the probe can be deduced therefore from the measured diffusion coefficient D by using the Stokes-Einstein relationship:

$$D = F(k_B T / 6\pi r \eta)$$

where r represents the probe diameter. Such an assumption is true unless selective pathways exist inside the system with sizes comparable to the size of the electrochemical probes, which is unexpected except for close to the xerogel state. However, if the electrochemical probes are linked to the polymeric skeleton, their diffusion behaviour will be representative either of the local motion of the polymers or oligomers, or of the kinetics of an electron exchange between neighbouring sites.

The first requirement to be met before undertaking such a study was to verify the validity of our former assumption, *i.e.* molecules embedded into inorganic gels are able to diffuse freely towards an electrode with a constant diffusion coefficient. To validate this, three electrodes were introduced at the same time into a silica gel loaded with ferrocenylmethanol, one classical 1 mm diameter microelectrode, and two ultramicroelectrodes, with 17 and 5 μm diameters, respectively. If chronoamperometry experiments are performed with such a device, a classical Cottrell law is expected and obtained for the solution just after mixing (gel time is *ca.* 12 h in this case) therefore the product $i(t^{1/2})$ is a constant which depends only upon the electrode parameters and allows normalization of the subsequent electrode response. When the experiment is repeated after gelation has taken place, it is possible to plot the normalized value Ψ (against solution value) of the product $i(t^{1/2})$ vs. time. Fig. 3 shows that a value of 1 is retained over more than 5 orders of magnitude. This leads to three important preliminary conclusions: first, a Cottrell law is retained inside the gel, which shows that the gel behaves effectively as a liquid. Secondly, the same law is retained over a very large time scale, *i.e.* the same diffusion law is followed in the gel for pathways in the range *ca.* 500–10 μm . Thirdly, the solution value remains constant and hence no selective pathway exists

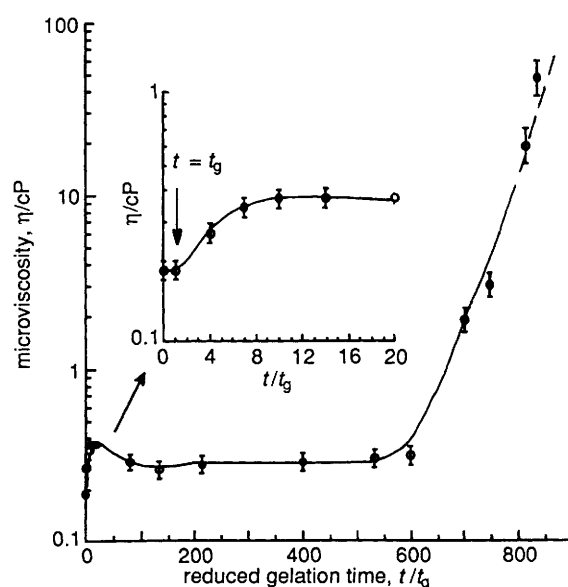


Fig. 2 Microviscosity experienced by an unsubstituted ferrocene probe in a silica TMOS gel (base catalysed, $t_g = 9$ mn) upon aging and subsequent drying; initial ferrocene concentration 10^{-2} mol dm^{-3} with 0.1 mol dm^{-3} TEAP added

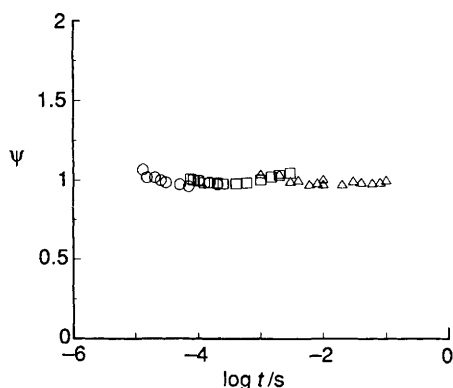


Fig. 3 Chronoamperometry of a silica gel (without catalysis) aged $2t_g$ (24 h), containing 10^{-2} mol dm^{-3} ferrocenylmethanol with 0.2 mol dm^{-3} TEAP added, recorded on different electrodes (\circ) 5 μm diameter gold, (\square) 17 μm diameter gold and (\triangle) 1 mm platinum. Variation of $\Psi = it^{1/2} FS_{\text{elec}} D_{\text{sol}}^{1/2} C^0$ with the measurement time. S_{elec} = surface area of the electrode, D_{sol} = diffusion coefficient of the solution. ($S_{\text{elec}} D_{\text{sol}}^{1/2}$ was measured for each electrode, just after mixing, by the variation of i with $t^{-1/2}$)

inside the gels, which can therefore be considered as isotropic for this investigation.

In addition, it should be pointed out that precise and reliable results can be obtained from such gels, as attested by the cyclic voltammograms that are represented in Fig. 4. It is clear that typical semi-infinite diffusion behaviour is obtained

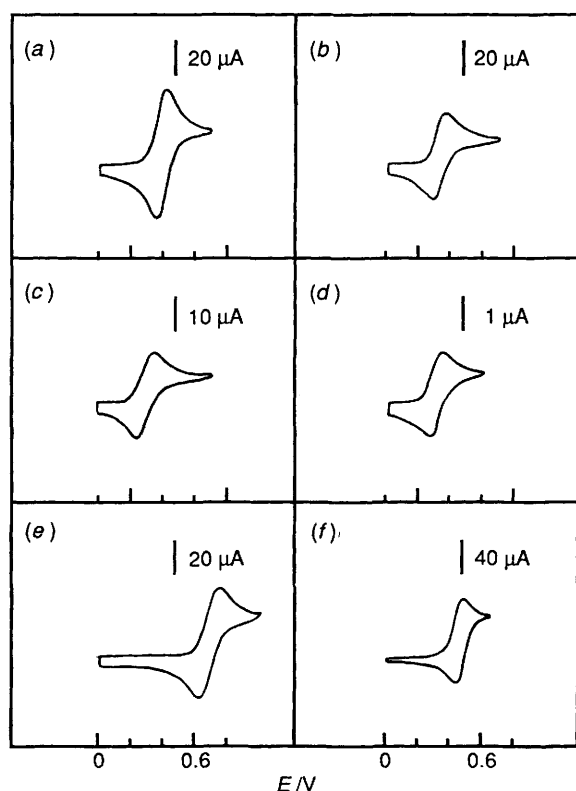
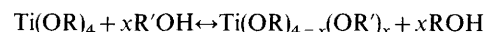


Fig. 4 Voltammograms recorded from: (a)–(d) silica gel (base catalysis) aged, respectively for (a) 0 min (at $t_g = 9$ min), (b) 2 days (ca. $300 t_g$, gel not dried); (c) 3 days (partially dried gel) and (d) 5 days (dried gel), probe ferrocenylmethanol (2×10^{-3} mol dm^{-3}) electrode, 3 mm diameter glassy carbon, scan rate 0.1 V s^{-1} , TBAP 0.1 mol dm^{-3} ; (e) titanium gel at $t_g = 30$ min, probe ferrocenylmethanol (10^{-2} mol dm^{-3}), electrode 1 mm diameter platinum, scan rate 1 V s^{-1} ; (f) silica gel (acid catalysis) aged $2t_g$ (24 h), probe FDA (2×10^{-3} mol dm^{-3}), electrode 3 mm diameter glassy carbon, scan rate 0.1 V s^{-1} , TEAP 0.1 mol dm^{-3}

in all cases and hence the gel is an excellent medium for such experiments. This confirms the result of our former work.⁸ We have also ensured that the nature of the electrolyte (TBAP or TEAP) had no apparent influence on the shape or size of the voltammograms, as could be expected.

The different absolute values of the diffusion coefficients for the different sol–gel systems studied are reported in Table 1. Both values in the sol and in the gel states are reported (gel values for $t = t_g$). The experimental error on the listed values is no better than 30% since the electrode is repolished or changed between experiments and its surface is known with poor precision only. However, the precision of the measure along a single experiment is considerably better and can be estimated within 5% (represented on Fig. 1). The general behaviour is that an important mobility is observed in all the systems studied with no difference between the sol and the gel when the molecules are not attached. Even after the macroscopic sol–gel transition, at the microscopic scale all gels behave like liquids. For the ferrocenylmethanol probe, the diffusion coefficient is lower in the titanium than in the silicon systems. This is the result of reactions between the hydroxymethyl-substituted ferrocene and the alkoxy groups of the titanium alkoxide precursor. Alcohol interchange reactions are known to occur when alkoxides are dissolved in alcohols other than the parent one.²² It has been demonstrated that hydroxylation is rather slow for silicon alkoxides and occurs only with an acidic catalyst²³ (this is confirmed by results given earlier in this paper). However, it is much faster in the case of transition-metal alkoxides. ⁴⁷Ti, ⁴⁹Ti NMR experiments have shown that hydroxylation of $\text{Ti}(\text{OR})_4$ occurs as soon as the alkoxide is dissolved into another alcohol.²³ Five different species corresponding to x ranging from 0 to 4 are formed as follows:



The titanium alkoxide species to which the probes are attached in this case are known to be oligomers and therefore diffuse rather slowly.² Note that a small decrease of the diffusion coefficient is also observed with larger free probes as copper(II) dimethylphenanthroline perchlorate (copper DMP) as it could be expected.

When the probes are strongly bonded (FDA or Fc-acac) the mobility at the gel point is still lower. In the case of titanium the diffusion coefficient is very low and there is no difference between the sol and the gel. This behaviour should be related to the fact that transition-metal alkoxides are a very reactive species that undergo very fast hydrolysis condensation reactions. Hence immediately after mixing, a large number of the ferrocene probes are anchored to large polymers and most probably do not contribute to the apparent diffusion coefficient. The small amount of freely diffusing probes gives

Table 1 Absolute values of diffusion coefficients of different substrates in the gels

compound	type of gel	diffusion coefficient/ $\text{cm}^2 \text{ s}^{-1}$
ferrocene	silica	2.9×10^{-5a}
	zirconium	1.2×10^{-5a}
	titanium	10^{-5a}
ferrocenylmethanol	silica	10^{-5a}
	titanium	10^{-6a}
copper(II) (DMP) ₂	silica	3×10^{-6a}
	silica	10^{-6} (sol)
FDA	silica	5×10^{-7} (gel)
Fc-acac	titanium	3×10^{-8} (sol and gel)

^a The same coefficient has been measured for free molecules in the sol and gel states.

an apparently low diffusion coefficient which reflects a drastic decrease in the concentration of diffusing molecules.

Beyond the absolute value of the diffusion coefficient, we also looked more closely at the relative variations of the diffusion coefficient (by examining the reduced diffusion coefficient D/D^0) with the time along the evolution of several types of gels (chemical evolution, drying).

Behaviour of Silica Gel Loaded with Free or Attached Electroactive Molecules

Behaviour of Gels Loaded with Free Molecules

We have investigated the kinetics of diffusion of ferrocene and ferrocenylmethanol into three kinds of gel with a base catalyst, with an acid catalyst or without a catalyst. The variation of the reduced diffusion coefficient (*i.e.* the diffusion coefficient normalized *vs.* its value for the sol D^0 to avoid reproducibility errors owing to electrode surface variations) is represented in Fig. 5. First, it can be said that, qualitatively, a similar behaviour is observed for all types of gel, apart from small variations which will be discussed. No variation of D/D^0 is observed at the gelation point, although the initial solution has solidified and no longer exhibits macroscopic flow. Thus, the electrochemical results show that the macroscopic rigidification of the sol is not accompanied by rigidity at the microscopic level. The solid phase causing the rigidity at the macroscopic level, and characterized by the divergence of the

macroscopic viscosity, represents only a small percentage of the total volume of the gel. The solvent phase at the gel point (alcohol and water) constitutes the largest volume fraction of the gel and at this stage the mobility of the ferrocene molecules is still completely free in the open structure of the gel. The second step of the process is the aging period. A decrease of D/D^0 is observed in all three cases. Such a phenomenon starts at *ca.* $t=3t_g$ and reaches a first plateau at a time of *ca.* $10-20t_g$. Concomitant diffusion of reactants and products is possible through the interstitial liquid phase of the gel, allowing hydrolysis and condensation reactions to continue. The electrochemical probe is not simply surrounded by the interstitial solvent as during the gelation stage, but must now be surrounded by percolating small oxypolymers.

For a longer aging period (between $t/t_g=20$ and $t/t_g=100$) in a closed vessel, the gel exhibits a slight increase of D/D^0 . Such an increase is probably related to depolymerisation reactions²⁴ or to the fact that small polymers located inside the porous structure can condense (stick to larger polymers) at the pore surfaces. This latter phenomenon must decrease the amount of polymeric species present in the liquid phase of the gel, and thus decrease the microviscosity experienced by the ferrocene probe. We have noticed that the acidic gels loaded with ferrocenylmethanol show relatively marked oscillations in the beginning of their evolution [Fig. 5(b)]. However this behaviour is lost when we come back to ferrocene, in which case a behaviour analogous to a neutral gel is obtained

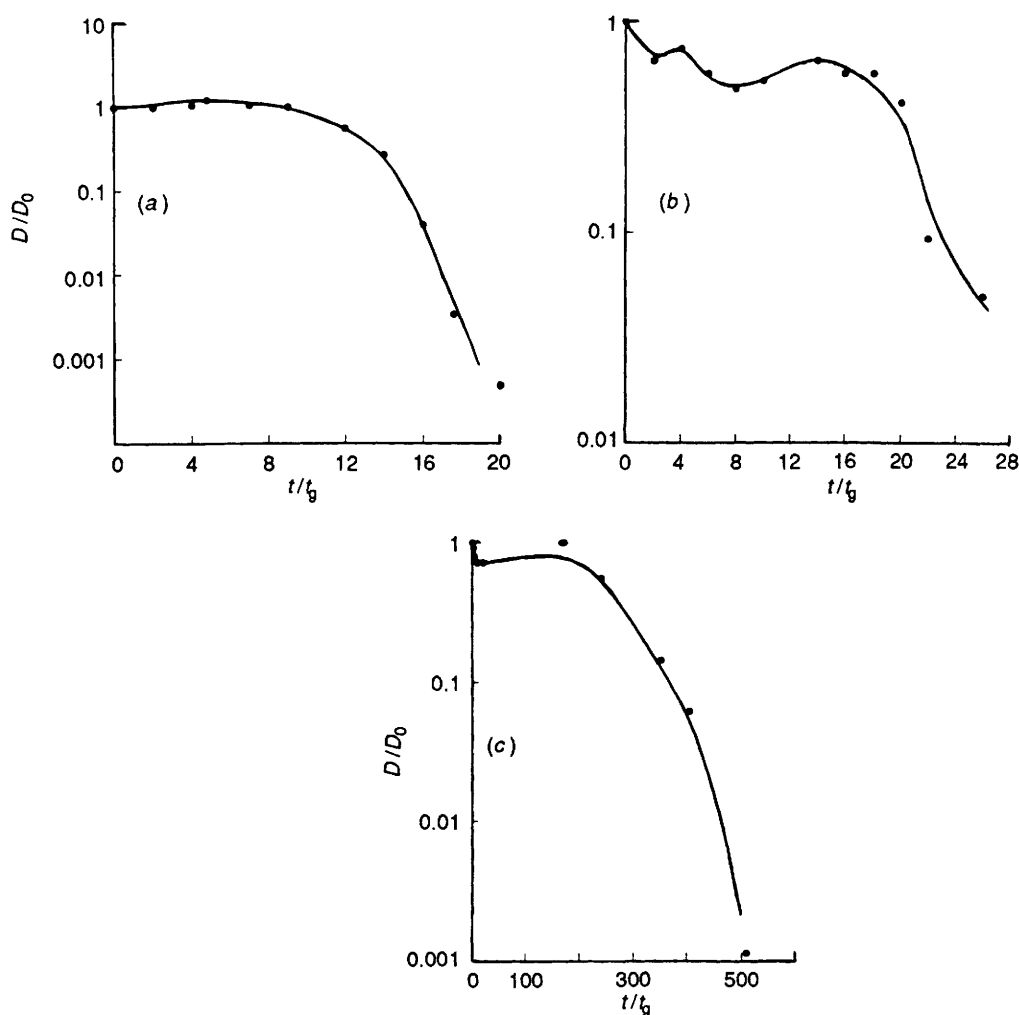


Fig. 5 Variations of the reduced diffusion coefficient (D/D^0) for silica gels in (a) no catalysis; (b) acid catalysis; (c) base catalysis. The probe was ferrocenylmethanol at a concentration of 10^{-2} mol dm^{-3} . A 3 mm diameter glassy carbon electrode was used for (a) and (b) and a mm platinum electrode for (c) (electrolyte TEAP 0.1 mol dm^{-3})

[cf. Fig. 5(a) and (c)]. This behaviour is observed in the case of an acidic gel with ferrocenylmethanol and is probably due to exchange of the ferrocene alcohol functionality with the methoxy groups on the silicon. As previously described, this reaction is slow for silicon alkoxides but is known to occur in the presence of acidic catalysis.^{22,23} It is true that the choice of ferrocenylmethanol may look a poor choice, but it is almost the only neutral molecule with a simple monoelectronic electron transfer at a convenient potential which was very soluble in aqueous alcohol. In addition, we have demonstrated that in the case of acid-catalysed polymerisation only the OH function introduces different probe behaviour with silica gels and we wish to avoid the use of charged electroactive probes as far as possible. (Although the behaviour of FDA does not appear to make a noticeable difference in this respect.)

D/D^0 reaches a plateau in which the diffusion coefficient of ferrocene is still quite high ($D/D^0 \approx 0.8$). This indicates that the fluidity around many ferrocene molecules is still quite high in the wet gel, even a long time after the sol-gel transition ($t > 100 t_g$ in the case of a base-catalysed gel). This behaviour has been observed previously from two-dimensional NMR⁴ and fluorescence measurements.⁵ Such phenomena might be better characterized by microviscosity which reflects the local friction between dye molecules, medium-sized polymeric species and solvent, moving inside the remaining porous texture of the gel. Thus changes of D can also be related to modifications of the microviscosity experienced by the ferrocene probe (Fig. 2). Upon air drying, the gel structure collapses and the gel shrinks continuously, the kinetics of shrinkage being closely related to the size of the openings which allow the solvent to evaporate. Once a certain point is reached, the diffusion coefficient drops drastically; at the last possible

measure the apparent value of the actual diffusion coefficient is then in the $10^{-8} \text{ cm}^2 \text{ s}^{-1}$ range. It is most probable that the drop is caused by the closing of the microdomains existing within the gel, and diffusion within the gels is restricted. At this point, it is difficult to say whether the molecules still diffuse, or if electrons are simply exchanged between fixed redox sites as in a classical modified electrode. It is possible to see the gel as a network of pools related by solvent-filled channels; when there is not enough remaining solvent to fill up the channels, electrons should hope to ensure the electrochemical process. However, another possible explanation is that a surface-adsorbed solvent layer remains on the polymer surface, which would still allow diffusion of electroactive species, although at a much slower rate. A useful, although long, experimental investigation would be to vary the concentration of the electroactive probes over a wide range and to note the differences that occur at given advanced dried stages. However, we were unable to undertake such an investigation owing to problems with experimental hazards and limitations of precision.

Note that the evaporation of the solvent must be very slow, otherwise the mechanical effects due to the electrodes are too strong and the gel breaks before the xerogel state can be reached. Generally it is sufficient not to close the cell too tightly; this allows evaporation of the solvent to give continuous drying, which never exceeds a period of 1 month. It is then the shrinkage relative to the initial volume, rather than time, which characterizes the stage of drying. Fig. 6 shows the relative dependence of the shrinkage of a silica gel as a function of drying time. The results show that in the case of silica gels, the characteristic drying time when D/D^0 drops, is the same whatever catalyst is employed. At the critical stage, the gel has lost the two-thirds of its initial mass (reaching ca. 30% of its initial mass). A similar shrinkage is observed in volume, which is expected since the gel is mostly composed of solvent even at a relatively advanced drying stage. It is worthy of note that the gel remains homogeneous through the entire drying process; the only limitation encountered is due to mechanical breakage around the electrodes, at an advanced drying stage.

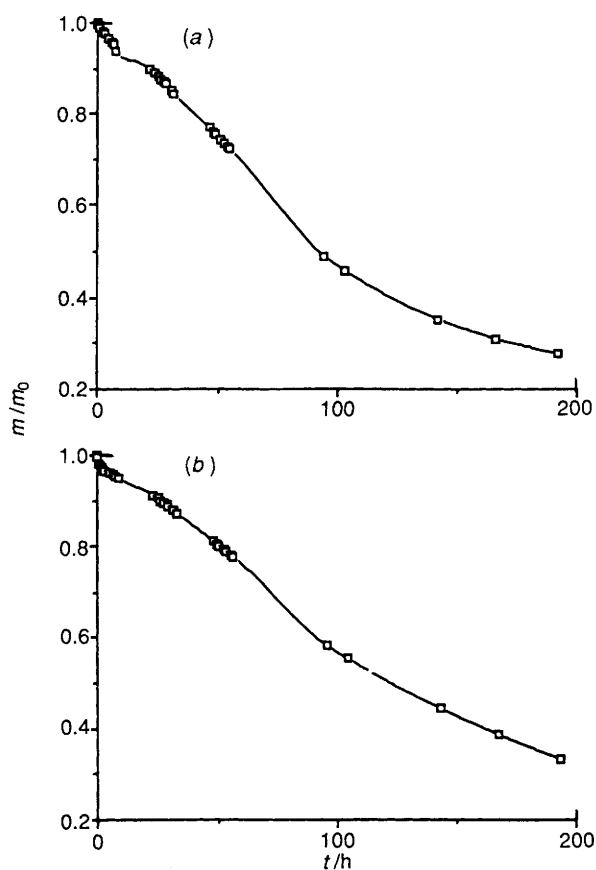


Fig. 6 Relative mass loss upon drying (in our experimental conditions) of silica gels (a) base catalysed; (b) without catalysis

Behaviour of Silica Gels Loaded with Bonded Molecules

We have only investigated the behaviour of gels made without catalysis or with an acid catalyst, because these were the most interesting to observe for both the gelation process (from the sol state) and the gel evolution. Long gelation times were the best conditions under which to study the evolution of the sol and of the freshly formed gel. We did not focus here on the drying process, since from our former experiments all silica gels apparently behave similarly upon drying. Fig. 7 shows the evolution of the reduced diffusion coefficient D/D^0 of FDA in both cases. In such a case chronoamperometry experiments are a helpful tool in studying sol evolution since D/D^0 decreases by more than a factor of two during the gelation process. It is likely that the ferrocene probes attach themselves to short-length oligomers, which accounts for the observed decrease. The variation of D/D^0 becomes less important when the gelation point is reached, because the average weight of the oligomers probably becomes more or less constant. While the shortest chains continue to aggregate and thus increase their average weight, the longest ones attach themselves to the infinite backbone and become immobilized this way. The oscillations attested by D/D^0 value are probably due to a competition between these two opposite effects; however, the observed maximum was rather weak.

The D value measured just after mixing for FDA is $10^{-6} \text{ cm}^2 \text{ s}^{-1}$, and is half this value at the gel point. Taking this into account, if the relative decrease of D/D^0 is proportional to an

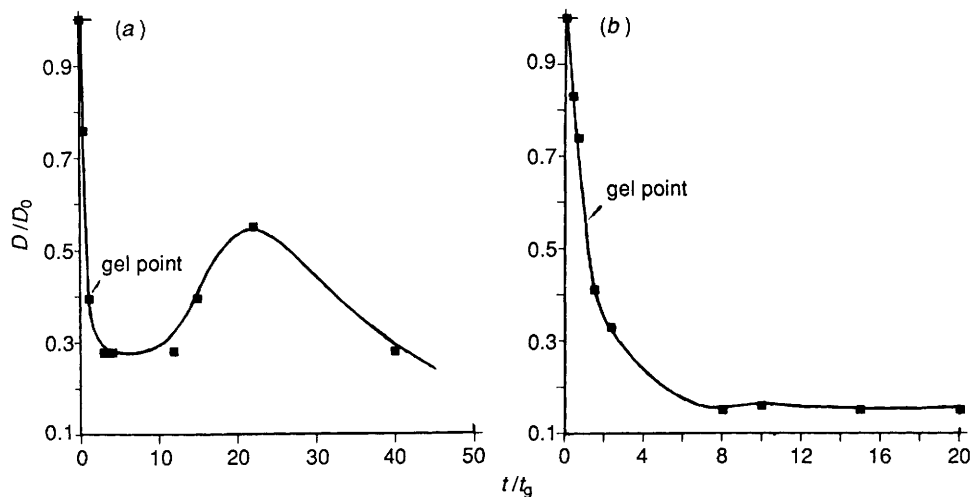


Fig. 7 Variation of D/D^0 of FDA (bound ferrocene) for silica gels; (a) without catalysis and (b) base-catalysed. FDA concentration = 2×10^{-3} mol dm $^{-3}$ and the electrode, 3 mm diameter glassy carbon (TBAP 0.1 mol dm $^{-3}$)

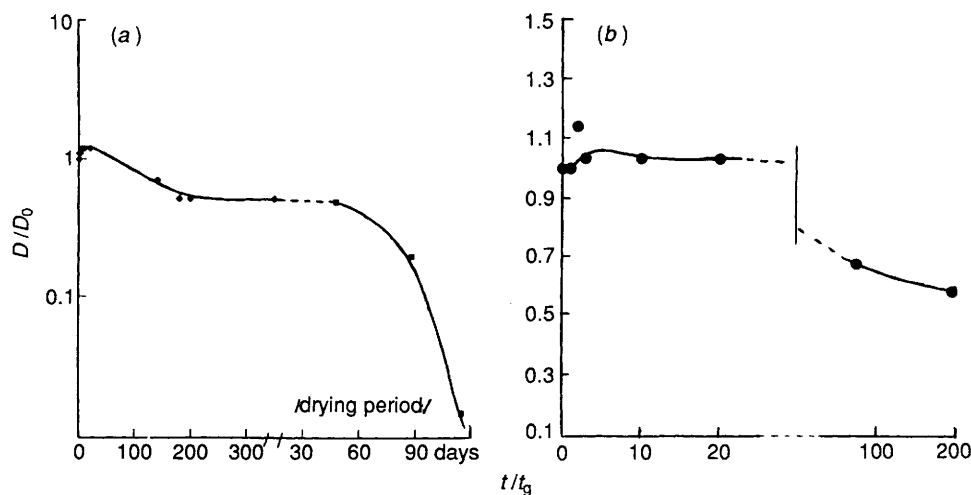


Fig. 8 Variation of D/D^0 of (a) ferrocenylmethanol (10^{-2} mol dm $^{-3}$) and (b) Fc-acac (3×10^{-3} mol dm $^{-3}$) in an acidic titania gel during the evolution of the gel and its further drying. Electrode, 1 mm diameter platinum. The absolute value of the diffusion coefficients is 30 times smaller in (b) than (a)

increase in weight due to polymerization reactions, the bigger polymers contribute only slightly to the apparent value of D/D^0 and the smaller species contribute for its main part. Therefore at the gel point, *ca.* 35% of the species are forming the larger polymers that contribute to the macroscopic sol-gel transition. Similarly ^{29}Si NMR²⁵ and small-angle neutron scattering experiments (SANS)²⁶ have also shown that a large amount of mobile species are still present at the gel point. All these data are in agreement with a polymerization process that produces a collection of branched polymers with a wide size distribution.²⁶ The smaller polymers which are more numerous, control the local densities of chain segment while the few larger ones are responsible for the macroscopic phenomenon of gelation.

Behaviour of Transition-metal Gels

The same means of investigation have been applied to explore the behaviour of titanium oxide and zirconium oxide based gels. With zirconium oxide gels a very stable signal can be observed with almost no variations with the first periods of the gelification process; D/D^0 continues to be constant during the first steps of the drying process, but after these preliminary stages the gel always cracks because of the mechanical effects due to the presence of the electrodes. Therefore we have not

been able to observe the decrease of D/D^0 which occurs at the end of the drying process. These observations are in agreement with rheological experiments²⁷ that metal oxide gels prepared in the presence of a large amount of complexing ligands (acac) behave as physical gels with very few crosslinking points.

In contrast, with the titanium gels prepared in acidic media which are more elastic and more crosslinked,²⁷ it has been possible to observe a qualitative behaviour similar to the silica gels. Fig. 8(a) represents the evolution of D/D^0 for ferrocenylmethanol in a Ti gel. Three steps can be distinguished: an initial very small rise followed immediately by a decrease and stabilisation at nearly the solution value (0–20 t/t_g); then a decrease during the first steps of the drying to *ca.* half the solution value; lastly, at *ca.* 75% drying of the initial gel the value of D/D^0 falls by a factor of 100 and finally no signal can be recovered from the gel. In such a case the drying process must be extremely slow to avoid cracking the gel; the average evaporation time chosen was *ca.* 3 months for *ca.* 10 cm 3 gel.

It is interesting to compare the behaviour of the same system, but with Fc-acac replacing the ferrocenylmethanol. In this case, the electroactive probe becomes strongly linked to the oligomers and the polymers *via* the complexation of the acac

group borne by the ferrocene with the Ti centres. It can be seen from Fig. 8(b) that the same qualitative behaviour is obtained for D/D^0 . However, a significant difference is noticeable, which is that the absolute D value of the linked ferrocene becomes very low, ca. $3 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$. This is further proof that high-molecular-weight species are formed early, which would account for this drastic initial drop in the diffusion coefficient. Comparing this last value with the value found for ferrocenylmethanol in titanium, a ratio of 30 is found between both cases. Therefore, we would have in this case 5–6 times less mobile species in the freshly formed sol than with the more readily exchangeable ferrocenylmethanol moiety. This result is in accordance with the polymerisation model already discussed,²⁶ a large number of high-molecular-weight polymers formed very quickly being in accordance with the well known, very fast polymerization rate of the transition-metal alkoxides.²

Conclusions

This paper addresses a detailed and general description of the electrochemical behaviour of either silica gels or transition-metal oxide based gels loaded with free, or chemically bonded, electrochemically active probes. The diffusion behaviour of these electrochemical probes throws light on the microstructure of such systems. Clearly, the free probes do not experience the sol–gel transition. The rigidification at the macroscopic level is not followed by a rigidification at the microscopic level. However, when the probe is chemically anchored to the precursor, the sol–gel transition can be detected clearly. Moreover, a comparison of the diffusion coefficient between the free species and the bonded species in the gel gives information on the nature and the number of the polymeric species in the sols and gels. This can constitute a new and useful approach to investigate the kinetics of polymerization processes that lead to sol–gel systems.

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