

MATERIALS CHEMISTRY COMMUNICATIONS

Electrochemical Probing of the Sol–Gel–Xerogel Evolution

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Chronoamperometry has been performed on ferrocene embedded in silica and zirconia gels. The diffusion coefficient of ferrocene was measured along the sol–gel–xerogel transformations. Such electrochemical measurements are a sensitive probe of the structural and textural changes occurring in the sol–gel process.

Keywords: Sol–gel processing; Ferrocene; Chronoamperometric probe

The sol–gel synthesis of glasses and ceramics has received a great amount of scientific and technological interest during the last decade.¹ Sol–gel chemistry is mainly based on inorganic polymerization reactions. Starting from molecular precursors such as metal alkoxides $M(OR)_n$ ($M = Si, Ti, Zr$), a macromolecular oxide network is obtained *via* hydroxylation–polycondensation reactions.² A variety of physical and chemical factors (*e.g.* temperature, pH, concentration of reactants, catalyst, chemical additives) influence the polymerisation process^{2,3} and thus the properties of the final glass or the final ceramic. A detailed understanding of the underlying polymer growth process and of the evolution of the gel texture upon gelation, ageing and drying is essential because the subsequent stages of the glass- or ceramic-making procedure depend strongly on the initial structure and texture of the gel and xerogel.^{1,3} Therefore, research is currently being carried out to study the physical and chemical transformations that occur during the sol–gel–xerogel transformations. Fluorescence polarisation,⁴ ²H NMR⁴ or rigidochromic fluorescent probes⁵ have been used to characterize silicon oxide based gels. Recently, cyclic voltammetry studies have demonstrated the feasibility of electrochemical experiments in gelling systems.⁶

This communication describes a convenient method to study the microviscosity of sol–gel systems based on chronoamperometric measurements performed on ferrocene molecules embedded in gels. Such measurements do not necessarily require transparent matrices or deuteriated solvents. The diffusion coefficient of ferrocene in different inorganic gels has been measured along the sol–gel–xerogel transformation. The microviscosity, η , experienced by the ferrocene probe all along the sol–gel transformation has been deduced from the diffusion coefficient, D , by using the Stokes–Einstein relationship, $D = k_B T / 6\pi r \eta$ (a mean size $r = 2.50 \text{ \AA}$ has been taken for ferrocene). Such measurements provide a sensitive means of probing the structural and textural changes that occur during gelation, ageing, and drying of silica and transition-metal oxide based gels. Ferrocene-doped silica gels (gel 1) with a convenient mechanical resistance, and short gelation time have been synthesized by hydrolysing tetramethoxysilane $Si(OMe)_4$ in the presence of a nucleophilic activator catalyst $SNaSi^7$ (DMAP = 4-dimethylaminopyridine) as follows. Tetramethoxysilane (TMOS) (0.01 mol) was dissolved in methanol (0.06 mol) containing ferrocene, $LiClO_4$ and DMAP as a catalyst. Pure water (0.07 mol) was then added and the mixture was stirred for 1 min. The concentrations of the reagents were adjusted to yield a final molar ratio of $TMOS:H_2O:CH_3O = 1:6:7$. $LiClO_4$ and ferrocene

concentrations were, respectively, 0.1 and 0.01 mol dm^{-3} . The sol gelled at $t_{gel} = 10 \text{ min}$ at $T = 21 \text{ }^\circ C$.

Ferrocene-doped zirconium oxide based gels (gel 2) have been prepared from $Zr(OPr^n)_4$ precursors chemically modified with acetylacetonone² as follows. $Zr(OPr^n)_4$ was dissolved in *n*-propanol containing ferrocene and $LiClO_4$, and acetylacetonone was added. The solution was hydrolysed by adding water dissolved in *n*-propanol (10% water by volume in *n*-propanol). The concentrations of the reagent were adjusted to yield a final molar ratio of $Zr:water:propanol:acetylacetonone = 1:10:3:0.5$. $LiClO_4$ and ferrocene concentrations were, respectively, 1 and 0.01 mol dm^{-3} . A gel was obtained within *ca.* 40 min at $T = 21 \text{ }^\circ C$. Voltamperometric experiments were performed on ferrocene ($[Fe] = 10^{-2} \text{ mol } dm^{-3}$, $[LiClO_4] = 10^{-1} \text{ mol } dm^{-3}$, Pt or Ag working electrodes, Ag wire quasi-reference). Ferrocene exhibits classical behaviour in sols, gels and xerogels (Fig. 1) featuring classical $1e^-$ reversible voltammograms, with peak currents decreasing in relation to the evolution of the diffusion coefficient of the species. As expected, the Cottrell law is followed with better accuracy in the gels than in classical solutions, since no deviations due to convection can be seen, even after long times. This allows an accurate calculation of the diffusion coefficient, D , for the ferrocene inside different sol–gel systems as a function of time. A typical plot (gel 1) of the reduced diffusion coefficient ($D_R = D/D_0$) of these gels *versus* time (t/t_{gel}) is shown in Fig. 2. Typical D values for silica and zirconia sols and the ensuing gels immediately after the gelation are reported in Table 1. They are close to those reported for ferrocene in acetonitrile ($D = 2.4 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$).⁸ No special variation of D is observed

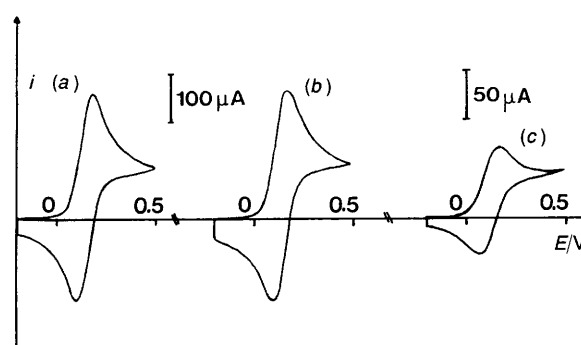


Fig. 1 Cyclic voltammograms at 100 V s^{-1} of the ferrocene embedded in the gels at three different characteristic times: sol ($t = 0$); gel point ($t = t_g$); partially dried gel ($t = 580t_g$)

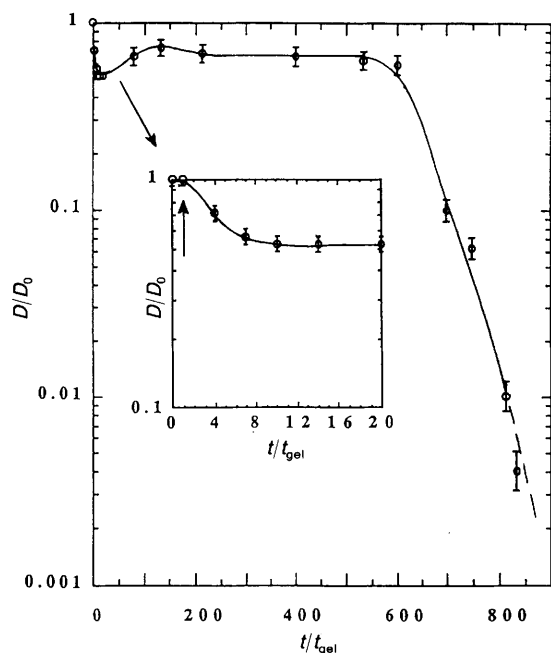


Fig. 2 Dependence of reduced diffusion coefficient of ferrocene in the gel on reduced gelation time for silica gel

Table 1 Diffusion coefficient of ferrocene in metal oxide based sols and gels

system	D_0 (sol)/ 10^5 cm 2 s $^{-1}$	D_0 (gel)/ 10^5 cm 2 s $^{-1}$
SiO $_2$ (gel 1)	2.9	2.9
ZrO $_2$ (gel 2)	1.2	1.2

at the gelation point although the initial solution has turned to a solid amorphous material which does not exhibit macroscopic flow. Thus, in the case of a solidification process caused by gelation, 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 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. At this stage, the mobility of the ferrocene molecules is not constrained by the open structure of the gel. Subsequently, the diffusion coefficient of ferrocene is about the same in the gel and in the liquid sol (Table 1).

The second step of the process is the ageing period. These experiments were performed on a slightly open cell (open diameter 0.5 cm) so that slow drying was allowed continuously. A decrease of the diffusion coefficient is observed. Such a phenomenon starts at *ca.* $t = 3t_g$ and reaches a first plateau at a time of *ca.* $10\text{--}20t_g$. Molecular transport of reactants and products is possible through the interstitial liquid phase allowing hydrolysis and condensation reactions to continue. The electrochemical probe is not simply surrounded by the interstitial solvent as during the gelation stage, but now interacts with small percolating oxo-polymers. Such results are in agreement with a polymerization process that produces a collection of branched polymers with a wide size distribution. The smaller ones, which are more numerous, control the local densities of chain segment, whereas the few larger ones are responsible for the macroscopic phenomenon of gelation.⁹ With increased ageing period ($t/t_g = 20\text{--}100$) in a closed vessel, the gel exhibits a slight increase of D_R . Such an increase is probably related either to depolymerisation reactions,¹⁰ which

lead to a partial depercolation of polymeric species, or to the fact that small polymers located inside the porous structure can condense (stick to larger polymers) at the pore surface. This latter phenomenon must decrease the number of polymeric species present in the liquid phase of the gel and thus decrease the viscosity experienced by the ferrocene probe.

Then D_R reaches a plateau in which the diffusion coefficient of ferrocene is still quite high ($D/D_0 = 0.8$). 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 ($t > 100t_g$). This behaviour has already been observed from ^3H NMR⁴ and fluorescence measurements.⁵ Such phenomena might be better characterized by microviscosity, which indicates only the local friction between dye molecules, medium-sized polymeric species and solvent moving inside the remaining porous texture of the gel. Thus, changes in D can be related to modifications of the microviscosity experienced by the ferrocene probe *via* the Stocke-Einstein relationship. After it has been air-dried, the gel structure collapses and the gel shrinks continuously. A strong and continuous decrease of the D_R (increase of the microviscosity) starts when *ca.* 40% of the liquid phase has been removed (Fig. 2). This step is accompanied by a progressive and eventually complete rigidification of the matrix. D can be measured even when > 70% of the liquid phase has been removed. Subsequent drying results in a porous solid called a xerogel. At this stage of drying, electrochemical measurements could not be performed.

The exploitable timescale on which our experiments were made is *ca.* 10–500 ms, which corresponds roughly to a mean free path, L [$L = (Dt)^{0.5}$], between 5 and 50 μm for the ferrocene molecule in the sol and gel. This shows that the ferrocene effectively has an extended motion over several pore diameters, and thus that these electrochemical measurements are probing changes in the distance travelled by the molecule as influenced by polymer growth. In the most aged measurable gel, this mean free path value falls by a factor of *ca.* 10, clearly showing the restriction of the molecular motion. Work is in progress to expand such measurements to a wide path range as well as to other silica- and titania-based gels. Moreover, the understanding of the structural and textural evolution of sol-gel systems can be improved greatly by using electrochemical probes of different size or probes chemically bonded to the alkoxide precursors.

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