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Electrochemical analysis of the sol–gel synthesis of phosphonate-modified titania through the diffusion of a functionalised ferrocene☆

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Abstract

Titanium oxide/phenylphosphonate hybrids were prepared by a two-step sol–gel processing, in the presence of ferrocenylphosphonic acid as an electrochemical probe. We showed that as expected the diffusion of the redox species was related to the kinetics of the sol–gel polymerization. The probable passage through cluster $Ti_4O(O^iPr)_8(PhPO_3)_3$ has been confirmed by the electrochemical response under partial hydrolysis conditions.

Keywords: Sol–gel; Electrochemistry; Phosphonate-modified titania; Redox probe

1. Introduction

During the last two decades, the development of organic–inorganic hybrid materials has been associated with the evolution of sol–gel process [1–3,7]. Furthermore, a wide class of hybrids involves the covalent bonding of the organic and the inorganic components through the use of coupling molecules [5,6]. The potentialities of phosphonate and phosphinate groups have been recently demonstrated in the coupling of organic components to metal oxides [4–6,8–10]. Actually, M–O–P and P–C bonds are quite stable towards hydrolysis and a wide range of functional phosphonate compounds is available.

Recently, metal oxide/phosphonate hybrids have been prepared by a two-step sol–gel process (Scheme 1), involving first the formation of M–O–P bonds by nonhydrolytic condensation of a metal alkoxide with a phosphonic acid and then the formation of the M–O–M bonds of the metal oxide network by hydrolysis/condensation of the remaining alkoxide groups.

The composition, the homogeneity, and the structure of the hybrid xerogels were previously investigated. Spectroscopic techniques, especially ^{31}P and ^{17}O MAS NMR ones, gave information on the mode of bonding of phosphonate units [10,11]. The intermediate sols were also studied by ^{31}P solution NMR to gain some insight into the condensation reactions involved in the first step of the sol–gel process [10]. Although NMR is a powerful technique, it lacks the possibility to investigate most kinetics, because the acquisition of spectra is usually relatively slow. Conversely, it was shown that electrochemistry could bring valuable information on sol–gel system, through interpretation of the measurement

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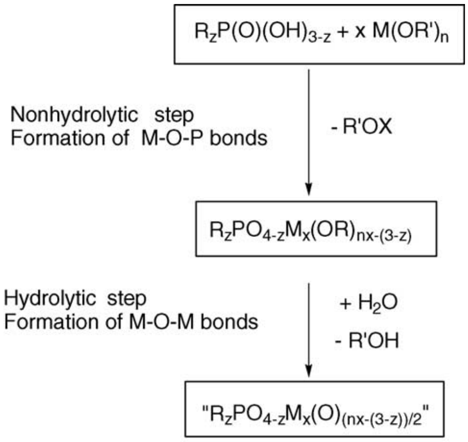
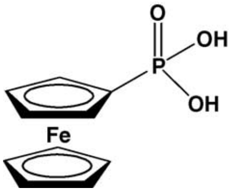


Scheme 1. Summary of the gels preparation.



Scheme 2. Structure of the ferrocenic probe.

of the transport of electroactive molecules in the medium [12–15]. The technique used, chronoamperometry, is a relatively fast technique, which allows to register one curve in less than a second. Both freely diffusing or on the contrary bound electroactive species can be used, although it is obvious that the species bound to the gel skeleton bring forth the most interesting information, since their diffusion is closely related to the oxopolymer motion dynamics, while free probes reflect only the interstitial solution microviscosity and therefore give only indirect information.

In the present work, we used ferrocenylphosphonic acid (FPA) (Scheme 2) as a probe to monitor the formation of $TiO_2/PhPO_3$ gels from titanium tetraisopropoxide and phenylphosphonic acid (PPA) precursors.

The diffusion of this probe, which should be tightly bound to the gel species, was investigated for different H_2O/Ti and P/Ti ratios.

2. Experimental

2.1. Chemicals

$Ti(O^iPr)_4$ (97%) was purchased from Aldrich and distilled prior to use. $PhPO(OH)_2$ (98%, Aldrich) was recrystallized from acetonitrile. Dimethylsulfoxide (DMSO) was distilled over CaH_2, dichloromethane was distilled over P_2O_5. Water was obtained from a Millipore-MilliQ system. All manipulations were carried out under an inert atmosphere. Ferrocenylphosphonic acid (FPA) was prepared by the method of Henderson [16]. Tetrabutylammonium perchlorate (TEAP) was purchased from Aldrich.

Table 1
Preparation of the hybrid gels from $Ti(O^iPr)_4$ and phenylphosphonic acid (PPA)

Sample	$Ti(O^iPr)_n$:$PhPO_3H_2$:H_2O	Aspect
Ti/P = 1/PPA	1:1:1	White opaque gel
Ti/P = 3/PPA	3:1:5	White opaque gel
Ti/P = 5/PPA	5:1:9	White opaque gel
Ti/P = 4/3/PPA	1.33:1:1.67	White opaque gel
Ti/P = 4/3/PPA	1.33:1:0.33	Cluster composition: non gelling sol

2.2. Preparation of the gels

Titanium oxide/phenylphosphonate hybrids with different Ti/P ratios were prepared from $Ti(O^iPr)_4$ and phenylphosphonic acid (PPA) precursors in two steps (Table 1). The concentration in the electroactive species, ferrocenylphosphonic acid (FPA), was about 5×10^{-3} M. In the first step, $Ti(O^iPr)_4$ was added under stirring to a solution of PPA and FPA in DMSO, and 0.1 M tetrabutyl ammonium perchlorate as supporting electrolyte salt leading to clear solutions. In all cases, the concentration of the metal alkoxide was 0.8 mol L^{-1}. It was checked that the electrolyte salt did not influence the sol–gel polymerization by controlling that the other parameters of the system remained constant, especially the gelling time. After stirring for 2 h at room temperature, the stoichiometric amount of water, previously diluted in DMSO so as to avoid local overconcentrations, was added at once or in two portions (25% first, then the remaining 75%) according to the series of experiments, leading to the formation of gels (Table 1). All experiments were carried out under argon atmosphere.

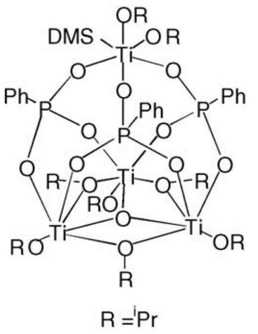
2.3. Electrochemical measurements

The electrochemical study of the polymer sols and gels was performed using a fast home made potentiostat [17] equipped with an ohmic drop compensation system, and connected to a Tacussel pilot and a Nicolet digital oscilloscope, with a 1 mm diameter platinum electrode. Pseudo reference was a silver wire.

3. Results and discussion

3.1. $Ti(O^iPr)_4$/PPA sol–gel diagram

The reaction of $Ti(O^iPr)_4$ with $PhPO(OH)_2$ (PPA) in DMSO (step 1) resulted in clear solutions whatever be the Ti/P ratio. The solutions obtained for Ti/P = 3 were previously studied by ^{31}P NMR spectroscopy [10]. When water (0.2 equivalent) was added the ^{31}P NMR spectrum showed



Scheme 3. Structure of the identified cluster in the 4:3:1 conditions.

a major resonance at 6.8 ppm. This resonance could be attributed to a molecular titanium oxo–alkoxo phosphonate. This compound could be crystallized from a DMSO solution and single-crystal X-ray diffraction led to the formula $Ti_4O(O^iPr)_8(PhPO_3)_3 \cdot DMSO$ and to the structure displayed in Scheme 3 [9].

The phase diagram (Scheme 4) of the PPA–TiO^iPr_4 system shows in addition that gels are obtained in a wide domain and that the amount of phosphonic acid employed can be relatively small.

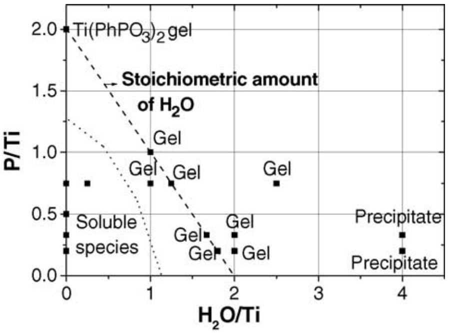
In this work, our aim was to test the ability of electrochemical techniques in following the entire course of the sol–gel polymerization, and in evidencing the formation of $Ti_4O(O^iPr)_8(PhPO_3)_3 \cdot DMSO$ cluster as a key step of the process whatever the P/Ti ratio.

3.2. Electrochemical results

TiO_2/PPA gel samples with different Ti/P ratios x were prepared, using a stoichiometric amount of water ($Ti/P/H_2O = x/1/2x-1$):

$$x\mathrm{Ti(O^iPr)_4} + \mathrm{PhPO_3H_2} + (2x-1)\mathrm{H_2O} \rightarrow \mathrm{Ti}_x(\mathrm{PhPO_3})\mathrm{O}_{2x-1} + 4x\,{}^i\mathrm{PrOH}$$

Two series of experiments have been performed. In the first series, the stoichiometric amount of water was added in one portion, whereas in the second series the water was added in two portions: the fourth of the stoichiometric amount first, then the other three-fourths after 1 h.



Scheme 4. State diagram for the $Ti(O^iPr)_4/PPA/H_2O$ system in THF.

In addition, one experiment was performed with the stoichiometry corresponding to the formation of the cluster ($Ti/P/H_2O = 1.33/1/0.33$):

$$4\mathrm{Ti(O^iPr)_4} + 3\mathrm{PhPO_3H_2} + \mathrm{H_2O} \rightarrow \mathrm{Ti_4(O)(PhPO_3)_3(O^iPr)_8} + 8\,{}^i\mathrm{PrOH}$$

In all cases, very well-defined voltammograms and chronoamperograms were obtained, as examplified on Figs. 1 and 2, which show the evolution of the electrochemical responses of the FPA redox probe in the gels in two selected cases. The FPA probe present before polymerization a reversible electrochemical response typical of a ferrocenic compound with $E_{1/2} = 0.81$ V versus silver wire reference electrode. The currents decrease steadily with the sol–gel polymerization time. This decrease has been ascribed to the decrease of the diffusion coefficient of the functionalized species in the sols and the gels [15]. Then we determined more precisely the relative variation of the diffusion coefficient with different concentrations of reactants (listed in Table 1), adding the stoichiometric amount of water either in one step or in two steps as mentioned above.

3.2.1. One-step addition of the stoichiometric amount of water

The top curve in Fig. 3a , corresponding to the cluster stoichiometry, is typical. Indeed, a stable stage is quickly reached ($D = 0.2D^\circ$) which corresponds to a hydrodynamic diameter of five times the one of the molecular ferrocenic probe ($D^\circ = 2.1 \times 10^{-6}$ cm^2/s), on the basis of the classical Stokes-Einstein law $D = kT/(6\pi\eta d)$, (with k is Boltzmann constant, T: temperature, η: viscosity, d is the hydrodynamic radius), which should be followed with objects like clusters. This is consistent with the formation of a stable, soluble, cluster with a relatively low molecular weight, and thus corroborates the previous studies on this system [10] that showed the major formation of $Ti_4O(O^iPr)_8(PhPO_3)_3 \cdot DMSO$.

When the stoichiometric amount of water is added in one step the gelation visually takes place in a few seconds. However, all curves (Fig. 3a) present two well-defined stages: first, a very sharp drop, up to a given stage, characterized by its diffusion coefficient, and then a much slower decrease in the diffusion coefficient, which reaches a final plateau stage. Thus, a very fast condensation occurs initially, leading to intermediate species with hydrodynamic diameters that appear to depend upon the Ti/P ratio: the lower the Ti/P ratio ($x = 1$ or 1.33) the smaller the intermediate species, which may be ascribed to the lower reactivity towards hydrolysis of the titanium alkoxide species modified by phosphonic acid. The same effect of chemical modifying has already been reported in the case of $Zr(OPr)_4$/acetylacetone systems [13]. It should be however remarked that the curves recorded for $x = 3$ and 5 are almost similar, showing that at low PPA content a similar highly condensed state is quickly reached. The second stage of the condensation, corresponding to the aging of the gel, is slower and the kinetics are very similar in all cases, which

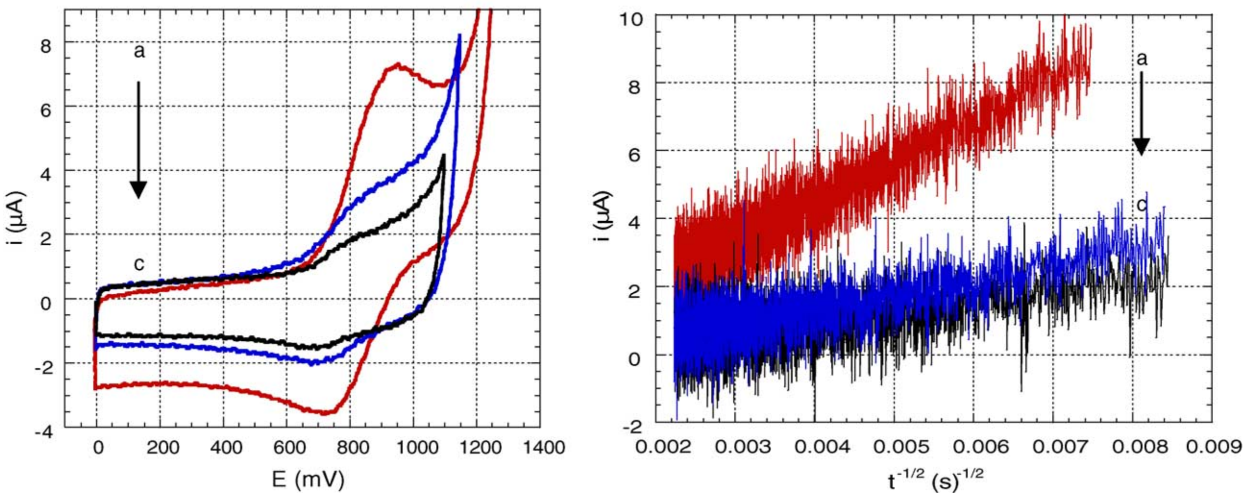


Fig. 1. Cyclic voltammetry ($\upsilon = 5$ V/s) during the sol–gel polycondensation after addition of one equivalent of water: (a) $t = 3$ min 30 s; (b) $t = 2$ h 10 min; (c) $t = 4$ h 29 min. Chronoamperometry during the sol–gel polycondensation after addition of one equivalent of water: (a) $t = 5$ min 10 s; (b) $t = 2$ h 12 min; (c) $t = 4$ h 31 min.

is in accordance with a lower reactivity of the intermediate species whatever be the remaining water content at this stage. Even after more than 4 h the diffusion coefficient remains high, which shows that the mobility of the species bound to the redox probe is still high. This suggests the incomplete condensation of the titanium species and the formation of a particulate gel rather than a polymeric gel. In addition, again the final state appears to depend mostly upon the Ti/P ratio, suggesting the limiting influence of phosphonic acid on the particle size. However, despite the presence of phosphonic acid, the overall polycondensation process is very fast, especially as compared with the kinetics of polycondensation of silicon alkoxides [15].

3.2.2. Two-step addition of the stoichiometric amount of water

When the water was added in two separate steps, a quite different behavior was observed. With only a quarter of the water stoichiometry, sols were obtained. The redox probe evidences a partially condensed state, which is quite similar to the previously observed cluster state (Fig. 3b). This behavior is consistent with the formation of titanium oxo–alkoxo

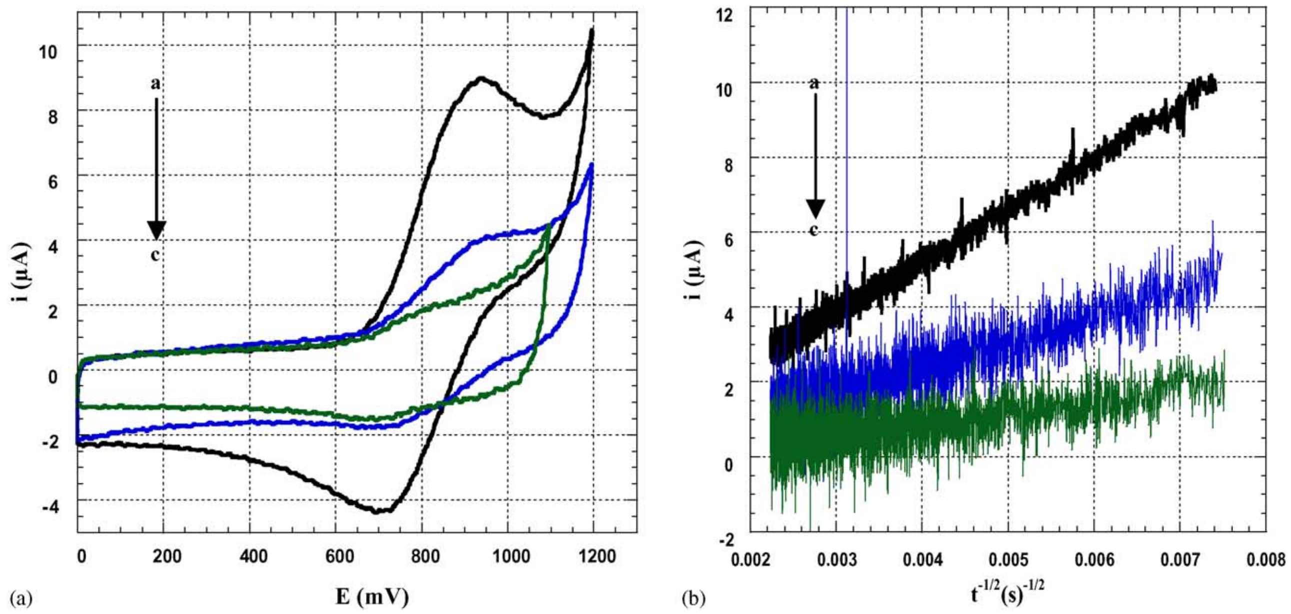


Fig. 2. Cyclic voltammetry ($\upsilon = 5$ V/s) during the sol–gel polycondensation Ti/P = 1/PPA, 1:1:1: (a) after addition of 0.25 equivalent of water $t = 58$ min; (b) after addition of one equivalent of water $t = 1$ h 07 min; (c) after addition of one equivalent of water 5 h 30 min. Chronoamperometry during the sol–gel polycondensation Ti/P = 1/PPA, 1:1:1: (a) after addition of 0.25 equivalent of water $t = 59$ min; (b) after addition of one equivalent of water $t = 1$ h 08 min; (c) after addition of one equivalent of water $t = 5$ h 32 min.

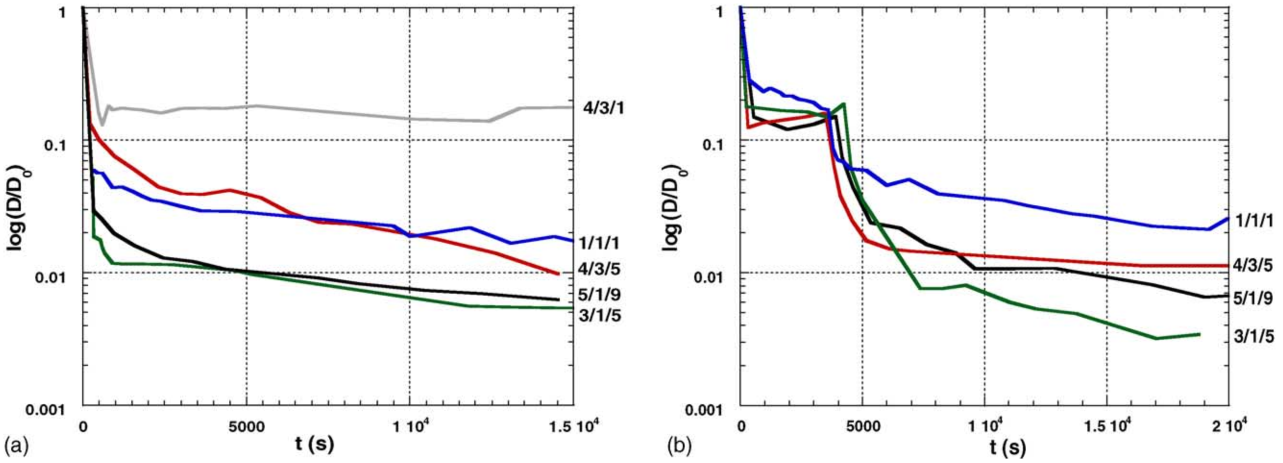


Fig. 3. Representation of the relative D/D° variation with time: (a) after one equivalent of water; (b) after 0.25 equivalent of water (cluster formation), one equivalent of water.

phosphonate clusters, labeled by the redox probe, along with titanium oxo-alkoxide clusters, the formation of which has been reported in the presence of a sub-stoichiometric amount of water [18]. These species (as a matter of fact $[Ti_7O_4](O^iPr)_{20}$ would formally result from the reaction of $0.25H_2O$ on $Ti(O^iPr)_4$) should not have hydrodynamic radii very different from the oxo–alkoxo phosphonate cluster $Ti_4O(O^iPr)_8(PhPO_3)_3{\cdot}DMSO$, thus, not modifying its diffusion conditions. This state appears quite stable, until further water addition is performed, which resumes the polymerization. Then, a behavior reminiscent of that observed above takes place, however leading to different final plateaus. This shows that (1) strong similarities exist between the condensed species formed at low water amount whatever be the initial composition, at least on the basis of the hydrodynamic radius, which should be correlated to the molecular mass, (2) the final state is determined by kinetic parameters and depends on the experimental conditions, such as the mode of adding water.

4. Conclusions

Electrochemical measurements have proved powerful to analyze the polymerization of phosphonate-modified titanium oxide gels. These measurements show that condensation occurs in two distinguishable stages, the first very fast leading to aggregates or clusters (among which the ubiquitous oxo–alkoxo phosphonate cluster), and the second much slower leading to the final gels, into which the mobility of the species remains important. Moreover the critical influence of the phosphonic acid as a chemical modifier in the sol–gel process has been confirmed.

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