Electropolymerization of carboxylic acid functionalized pyrrole into hybrid zirconium–silicon oxopolymer sol–gel coatings

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We describe the preparation of new hybrid materials using a novel method previously reported by us. These materials are constituted of an organic part and an inorganic network of silicon and zirconium oxopolymers. The organic polymer is obtained by electropolymerization of an N-functionalized pyrrole entrapped in the xerogel. The latter was obtained from a sol prepared by hydrolysis condensation of a mixture of alkoxysilanes, zirconium alkoxydes and the organic monomer. The chemical and electrochemical conditions to prepare these hybrid materials were investigated by varying the zirconium content, the presence and the nature of doping species in the xerogel, the nature of the electrolytic salt and the hydrolysis catalyst. From the results of cyclic voltammetry, optical microscopy, scanning electron microscopy and X-ray fluorescence, we show that the formation of a conducting polymer with good properties in the xerogel depends on the zirconium content and on both the nature and the presence of doping species in the xerogel, whereas the influence of the electrolytic salt is very limited.

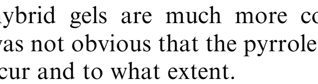
The preparation of conducting polymer-based hybrid materials is an important and interesting challenge because it allows to ally the mechanical and thermal resistance of the inorganic matrix[1,2] to the electrical properties of the conducting polymers.[3–5]

In part 2 of this work,[6] we described an original method to prepare such materials. It consists of the electrochemical polymerization of pyrrole derivatives into xerogels composed of zirconium oxopolymers. These organic compounds played a triple role. They allow the organic part to be anchored on the inorganic matrix, while in the same time they participate in the elaboration of the inorganic network, by controlling the reactivity of the zirconium alkoxides.[2,7–9] Finally, they allow the formation of the conducting polymer into a xerogel, through the polymerization of the anchored pyrrole rings in the hybrid xerogel.

In our earlier work on pure zirconia gels,[6] we showed that in the case of the carboxylic acid functionalized pyrrole, acetic acid must be added in order to stabilize the sols because of the weak complexing power of the conducting polymer precursors. Moreover, for some compositions, the formation of cracks in the inorganic network was revealed. Therefore, we chose to prepare pyrrole-functionalized silica–zirconia mixed hybrid xerogels, in which the zirconium and silicon oxopolymers are associated. Indeed, the groups of Wilkes,[10] Mark[11] and Sanchez[12] have studied and characterized the xerogels composed by polydimethylsiloxane (PDMS) and silicon or transition metal alkoxides. Sanchez *et al.*[12] show that zirconium and silicon oxopolymers are bound to each other by stable Zr–O–Si bonds. PDMS could be pre-formed or prepared *in situ*. Babonneau[13] studied the copolymerization at a molecular level. The differences in the reactivity of each precursor demand an accurate control of the reaction parameters. The length of the inorganic polymers depends on the molar ratio of each alkoxide in the mixture as well as on the polymerization process.

The preparation of these materials is easier to control because the zirconium alkoxides react with pre-hydrolyzed species that are less reactive. The hybrid materials synthesized according to this protocol exhibit excellent mechanical properties. Since our former study had shown that electropolymerization of pyrrole was compatible with zirconia gels, it was a desirable extension to investigate the same process in hybrid silica–zirconia gels, in particular due to their better mechanical properties. It is also clear that, given the relatively different structure of the final xerogels (the hybrid gels are much more covalently cross-linked[12,13]), it was not obvious that the pyrrole polymerization would easily occur and to what extent.

On the basis of the previous works, we prepared sols by acidic or neutral hydrolysis of diethoxydimethylsilane (DEDMS) in propanol, of triethoxymethylsilane (TEOMS) and of a mixture of zirconium tetrapropoxide [$Zr(OPr)_4$] and **6CA** (an acid functionalized pyrrole in which the acid group and the pyrrole ring are bound through a hexamethylene chain). Despite its slower kinetics, the neutral hydrolysis was investigated, because it was expected to be much less harmful towards the pyrrole ring.



6CA

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We have analyzed the influence of the zirconium content and of the catalyst on both the gelation process and the properties of the resulting xerogels, as well as on the electrochemical behavior of the hybrid material. We especially focus here on the conditions of formation of poly(**6CA**) into a xerogel (presence and nature of both the doping species in the xerogel and the salt in the electrolytic solution).

Experimental

Preparation and deposition of the hybrid gel layer

The sol precursor of the gel layer was prepared as follows: to 1.5 mL of diethoxydimethylsilane (DEDMS) in 3 mL of 1-propanol, are slowly added 0.5 mL HCl or H_3PO_4 (0.1 N) under vigorous stirring. The stirring is maintained for 20 min, after which 2.5 mL of triethoxymethylsilane (TEOMS) are added, and the stirring continued for 1 h. Finally, 3 mL of a mixture composed by x mL of $Zr(OPr)_4$ (70 wt % solution in 1-propanol), 0.250 g (1.10 mmol) **6CA** and $(3-x)$ mL of 1-propanol are added (Table 1). The volume of zirconium propoxide, x, is comprised between 0.40 mL (for SZ12C sol) and 2.50 mL (for SZ2C sol) according to the desired sol. The solution is further stirred for 15 min.

The hydrolysis could be performed by the addition of 0.5 mL of neutral deionized water instead of 0.5 mL of acidic water. But the period between each addition must then be multiplied by 3 because of the great decrease of the reaction rate.

The resulting viscous sol is highly stable and can be kept up to one week at room temperature (and much more if stored at low temperature). When the sol is applied with a pencil brush on an indium tin oxide (ITO) electrode, it gels in about one hour, then it is hardened by thermal treatment at moderate temperature (70 °C for 14 h) and reduced pressure (15 mm Hg), which eliminates all volatile compounds to leave a smooth xerogel. When desired, lithium perchlorate is added to the sol ($[LiClO_4]_{sol} = 0.1$ mol L^{-1}) before coating, in order to enable the electropolymerization.

Characterization of the deposits

The thickness of the deposits has been evaluated with scanning electron microscopy (SEM). The xerogel layer has a thickness of 20 μm (± 0.5 μm), however, the uncertainty on this value is important due to the deposition process. At each step of a process (before and after electropolymerization), the deposits have been observed by optical microscopy (Zeiss Axiotech, fitted with a Sony DXC 107AP CCD camera) and SEM (JEOL JSM 5600). Similarly, X-ray fluorescence experiments have also been done using a Fisherscope XRAY 1600 apparatus in order to study the evolution of the h_{Zr}/h_{Sn} ratios between each step (h_{Zr}, h_{Sn} represent the height of the zirconium and tin peaks observed in the spectra). The zirconium peak is specific to the xerogel whereas the tin peak characterizes the ITO electrode and its height remains constant.

The adhesion tests on the coatings have been performed before and after electropolymerization according to the French standard (T30-038), in order to estimate the adherence of the xerogel on the ITO electrodes. Incisions are made with a cutter, and a calibrated adhesive tape is then stuck on the deposit. The tape is pulled off, and according to what remains on the electrode and on the tape, the adherence is estimated on a 0 to 5 scale (0 corresponds to nothing on the tape, the best possible adherence, and 5 to more than 35% of the coating on the tape).

Electrochemical set-up

Polymerization experiments were performed in a one-compartment cell fitted with a saturated calomel reference, a platinum counter electrode with a 5 cm^2 area and as working electrode a coated ITO electrode prepared as above (area: 1 cm^2). The electrochemical apparatus was a PGZ 301 potentiostat (Radiometer) monitored by a personal computer using Voltamaster 4 electrochemical software. All potentials refer to the saturated calomel electrode (SCE). The films were prepared at a constant potential of +1080 mV. The solvent was distilled water, with 0.1 mol L^{-1} lithium perchlorate as the electrolyte salt. However, the electrochemical cycling of the films was carried out in acetonitrile containing 0.1 mol L^{-1} $LiClO_4$ at a scan rate of 50 mV s^{-1}. The charge used to form the films was determined by integration of the polymerization currents.

Table 1 Summary of the characteristics of the sols and the corresponding xerogels prepared from **6CA** before and after electropolymerization. A stands for adherence of the coatings

	Composition						
Type[a]	**6CA**/Zr[b]	Si/Zr[c]	H_2O/Si	Gel appearance after deposition	A	Gel after electropolymerization[d]	A
SZ2C	0.60	2.00	1.32	Opaque and cracks	5	More cracks	5
SZ3C	1.00	3.33	1.32	Turbid to opaque	2	No change $I_{max} \sim 3.5$ μA; $t(I_{max}) \sim 800$ s	3
SZ5C	1.50	5.00	1.32	Turbid	1	Uniform black coloration $I_{max} \sim 90$ μA; $t(I_{max}) \sim 900$ s	1
SZ10C	3.00	10.0	1.32	Transparent	0	Uniform black coloration $80 < I_{max} < 250$ μA; $50 < t(I_{max}) < 150$ s	0
SZ10N	3.00	10.0	1.32	Transparent	0	Uniform black coloration $I_{max} \sim 60$ μA; $t(I_{max}) \sim 200$ s	0
SZ10P	3.00	10.0	1.32	Transparent	0	Uniform black coloration $I_{max} \sim 180$ μA; $t(I_{max}) \sim 50$ s	0
SZ12C	3.60	12.0	1.16	Transparent	0	Uniform black coloration $I_{max} \sim 350$ μA; $t(I_{max}) \sim 200$ s	0

[a] In the gel nomenclature, SZ indicates that the sols and the corresponding xerogels contain silicon and zirconium oxopolymers. The number represents m, the Si/Zr weight ratio. In the last position, C and P stand for hydrochloric acid and phosphoric acid, respectively, added as hydrolysis catalyst, while N indicates that no catalyst was added. [b] [**6CA**] is the same in each sol: [**6CA**] = 0.105 M. [c] Weight ratio, $m = [DEDMS + TEOMS]/Zr(OPr)_4$. [d] The xerogels contain $LiClO_4$. The formation of poly(**6CA**) is not observed if the xerogel does not contain $LiClO_4$ ($I < 5$ μA for 1200 s).

Results and discussion

Preparation of the xerogels

The xerogels were obtained from sols deposited on the electrode surface. Gelation occurs quickly (within 1 h), due especially to fast solvent evaporation. Then the gels were hardened by a moderate thermal treatment to give the resulting xerogels (see Experimental).

The first step of the elaboration of the sols consists in the hydrolysis of DEDMS, the least reactive of the three alkoxides. PDMS chains are then formed by condensation of the hydrolyzed precursors. Afterwards, TEOMS is added and reacts with residual water and hydroxy groups at each end of PDMS. TEOMS acts as a cross-linking agent. As the added water amount is smaller than the stoichiometric one ($n_{H_2O}/n_{EtO} = 0.40$ instead of 0.50; EtO for ethoxy group), there is no water left when the mixture [$Zr(OPr)_4$ + **6CA**] is introduced. The complete hydrolysis is, however, performed during the gelation by air moisture, which provides the missing water. In this case, **6CA** ensures only the anchorage of the conducting polymer on the inorganic network. Seven sols were prepared. They differ in the zirconium content and the catalyst content. In every case, the concentration of **6CA** has been chosen to be the same: [**6CA**] = 0.105 M (Table 1).

Influence of the zirconium content. The relevant parameter determining the mechanical properties and the final aspect of the gels has been found to be the mass ratio [DEDMS + TEOMS]/$Zr(OPr)_4$. When this ratio is lower than 5, the sols are less stable and the xerogels obtained are no longer transparent, only weakly adherent and often cracked. The xerogels SZ10C and SZ12C exhibit the best features: they are transparent and very adherent (Table 1). The addition of $LiClO_4$ (0.1 M) has no effect on the appearance of either the sols or the xerogels. The water content and the polymerization time of the silicon alkoxides are also important. Working above the water stoichiometry results in the presence of excess water that may lead to the precipitation of zirconium oxopolymers upon the addition of $Zr(OPr)_4$. Moreover, the precipitation observed when the mass ratio Si/Zr is lower than 5 (*i.e.*, the content of zirconium propoxide in the sol is important) arises from formation of zirconium oxopolymer aggregates. As the ratio **6CA**/Zr decreases when zirconium content increases (Table 1), the polymerization of zirconium propoxide is more difficult to control.

Influence of the catalyst. The influence of the presence and the nature of the catalyst used during the first step (silicon alkoxide polymerization) on the stability of the sols and the aspect of the xerogel were studied. Three experimental conditions were tested, leading to the following gels: SZ10C (HCl as catalyst), SZ10P (H_3PO_4 as catalyst) and SZ10N (no catalyst was added).

The preparation of the sols SZ10C and SZ10P is similar, except for the type of acid added. However, in the case of SZ10N, although the process remains identical, the time intervals between each addition have been increased by a factor 3 because of the slower water consumption. The rate of hydrolysis-condensation of DEDMS in the absence of the catalyst drastically decreased.[2] The sols SZ10N are more stable than SZ10C and SZ10P: they can be stored for three weeks at room temperature instead of one week for the other two. The optical and scanning electron microscopy as well as the adherence tests reveal no difference between the behavior of these three types of xerogels (Table 1).

Electropolymerization of 6CA in the xerogels

Influence of the composition of the xerogel. In our previous work, we determined the best conditions for formation of poly(**6CA**) by electropolymerization of **6CA** entrapped in a xerogel. Similarly to the case of pure zirconia gels, in the silica–zirconia gels the growth of poly(**6CA**) is again observed only if $LiClO_4$ is present in the xerogel. The high electrolysis current values ($I > 60$ μA; Fig. 1 and Table 1), the appearance of a black coloration in the immersed part of the xerogel (Fig. 2) and a cyclic voltammetry (CV) response characteristic and significant of poly(**6CA**) (Fig. 1 and Table 1) confirm the formation of the conducting polymer. However, when the gel has a high zirconium content (case of SZ2C and SZ3C), the formation of poly(**6CA**) is impeded. This is attested to by the electrolysis currents and CV responses, which are weak ($I < 5$ μA; Fig. 3 and Table 1).

The xerogels SZ10 and SZ12C exhibit the most interesting results: the excellent adherence observed before electropolymerization is conserved and the material is not damaged by the electrochemical process according to the microscopic (OM and SEM) examination and the X-ray fluorescence experiments. In every case, h_{Zr}/h_{Sn} displays no variation before and after electrolysis: this shows that no degradation nor solubilization of the inorganic part of the composite takes place during the electropolymerization reaction, that is, electropolymerization is compatible with the sol–gel chemistry of

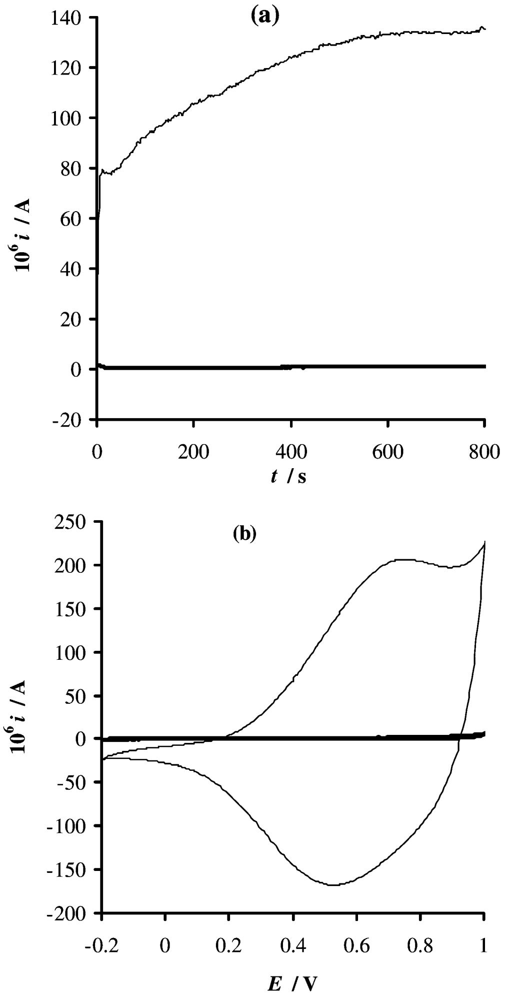

Fig. 1 (a) Electropolymerization curves $i = f(t)$ and (b) corresponding cyclic voltammetry curves related to the electropolymerization of **6CA** in SZ10C without $LiClO_4$ (thick line) or with 0.1 mol L^{-1} $LiClO_4$ added in the corresponding sol (thin line). The electropolymerization of **6CA** in an ITO electrode-deposited xerogel was performed in aqueous solution containing 0.1 mol L^{-1} $LiClO_4$ at 1080 mV. Cyclic voltammetry experiments were carried out in acetonitrile solution containing 0.1 mol L^{-1} $LiClO_4$, cycling between −200 and 1000 mV at a potential sweep rate of 50 mV s^{-1}.

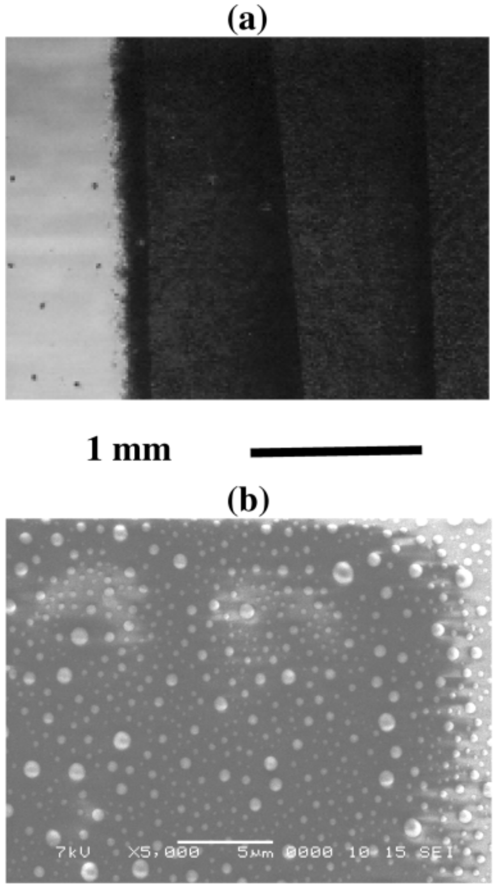

Fig. 2 (a) Optical (×50) and (b) SEM micrographs (×5000) after electropolymerization of **6CA** in SZ10C with 0.1 mol L^{-1} $LiClO_4$ added in the sol. The light-colored zone at the left of the optical micrograph represents the part of the coating that was not immersed in the electrolytic solution (not electropolymerized) whereas the dark zone at the right corresponds to the part of the coating immersed in the electrolytic solution (subjected to electropolymerization).

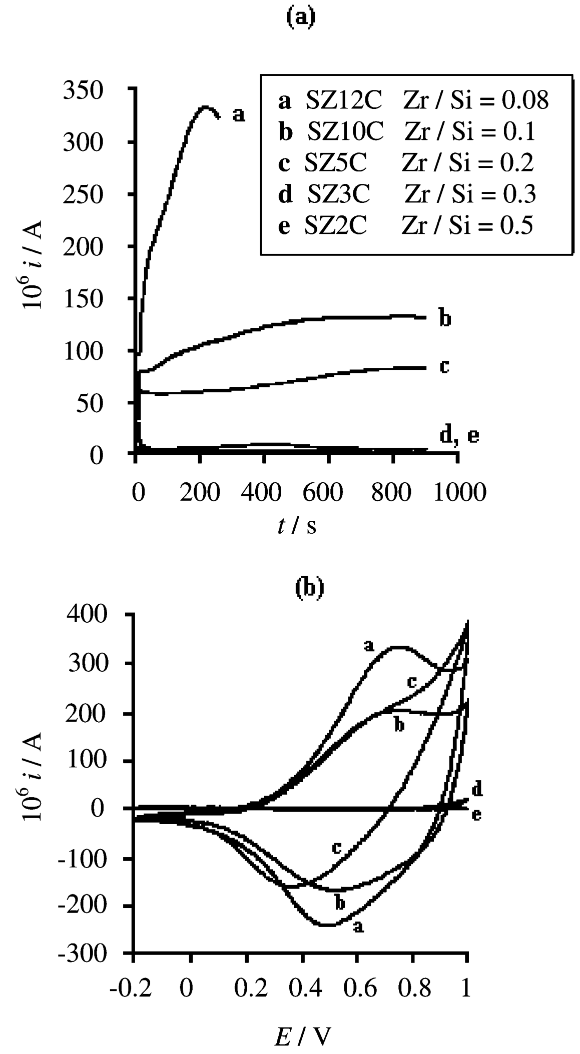

Fig. 3 Influence of the zirconium content: (a) electropolymerization curves $i = f(t)$ and (b) corresponding cyclic voltammetry curves after electropolymerization of **6CA** in the xerogels SZ2C, SZ3C, SZ5C, SZ10C and SZ12C. Electropolymerization conditions as for Fig. 1.

our types of gels. Moreover, the quality of poly(**6CA**) in SZ10C and SZ12C seems to be very good because the CV response is quite stable (more than 50 cycles) and reversible. The peak current values are relatively high: I is around 100 and 400 μA for SZ10C and SZ12C, respectively (Fig. 4). Because of the high electrolypolymerization current values, the duration of the electrolysis is short (between 100 and 250 s).

SZ5C displays an intermediate behavior: duration of electrolysis must be longer to obtain poly(**6CA**) (1000 s *versus* ~200 s). The conducting polymer prepared in SZ5C displays a weaker stability and a more important gap between peak potentials (Fig. 3).

Influence of the catalyst. Its influence on the electropolymerization of **6CA** is moderate. Indeed, in the case of SZ10C, SZ10P and SZ10N, poly(**6CA**) is easily obtained (Fig. 5 and Table 1). SZ10C displays a different behavior during the electrolysis and CV whereas the behavior of SZ10N and SZ10P are similar, and the conducting polymer appears to be of a lower quality. However, the gap of the peak potentials of poly(**6CA**) obtained in SZ10N and SZ10P ($\Delta E = 400$ mV) is more important than the gap observed for poly(**6CA**) in SZ10C ($\Delta E = 200$ mV). This is relatively surprising, because the presence of residual chloride ions in SZ10C probably disturbs the electropolymerization process more than in the other cases.[14]

Influence of the salt in the electrolytic solution. The electropolymerization of **6CA** in the xerogels was carried out from an aqueous solution containing $LiClO_4$. The replacement of this salt by another one [sodium tosylate ($C_7H_7NaO_3S$, NaTsO), sodium salicylate ($C_7H_5NaO_2$, NaSal), sodium oxalate ($Na_2C_2O_4$, NaOx), potassium nitrate (KNO_3)], where the anion is a well-known doping species of polypyrrole,[4] does not stop the formation of poly(**6CA**) in the xerogel SZ10C. For each salt, the immersed part of the electrode darkens and the CV response is significant (Fig. 6). However, often a greater gap and a cathodic shift of peak potentials are observed. This is most striking in the case of KNO_3 (Table 2).

According to these observations, the replacement of $LiClO_4$ in the electrolytic solution by other salts does not prevent the electropolymerization of **6CA** in the xerogel SZ10C and the influence on the quality of the polymer is moderate. This is of interest in the case of large surface coatings, since many salts are much cheaper than $LiClO_4$.

Influence of the nature of the doping species. Electropolymerization of **6CA** provides a conducting polymer if the xerogel contains $LiClO_4$. We tried to determine the effects of its replacement by other salts like tetraethylammonium perchlorate, $N(Et)_4ClO_4$, sodium tosylate, sodium salicylate, sodium oxalate or potassium nitrate. The anionic part of each salt is usually a possible choice for the doping of polypyrrole. The concentration of the salts and the conditions of electropolymerization were identical.

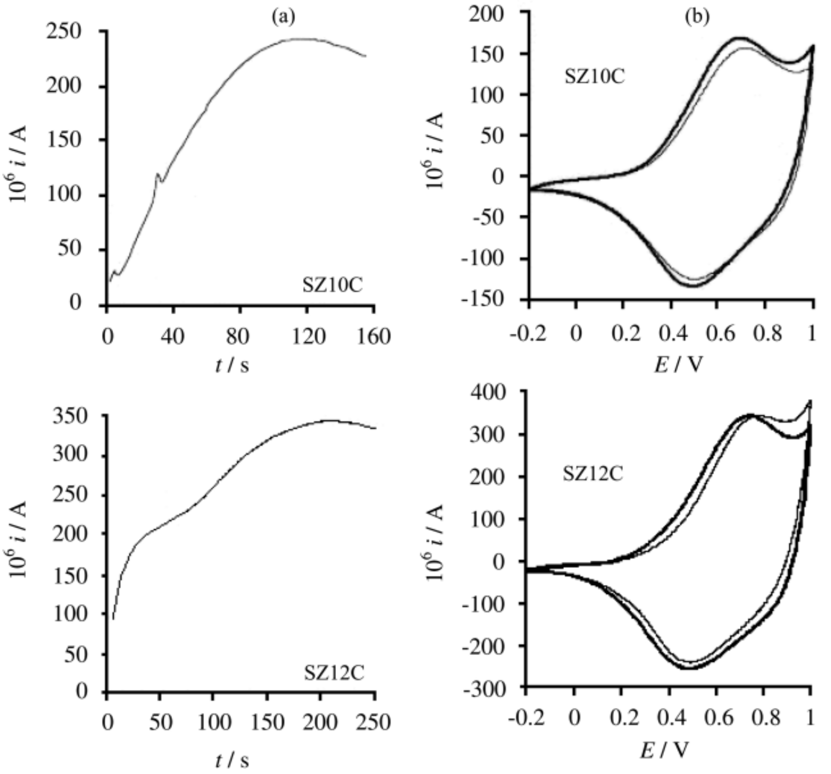

Fig. 4 Stability of poly(**6CA**). (a) Electropolymerization curves $i = f(t)$ and (b) corresponding cyclic voltammetry curves after electropolymerization of **6CA** in the xerogels SZ10C and SZ12C containing $LiClO_4$. The thick line is the first scan and the thin line the 50th scan. Electropolymerization conditions as for Fig. 1.

The replacement of $LiClO_4$ generates no modification of the aspect of the sol and the xerogel before the electropolymerization, except in the case of sodium salicylate and potassium nitrate. The sol SZ10C, originally colorless, becomes pale yellow after addition of sodium salicylate. Salicylate anion is a very strong complexing agent of zirconium atoms. This complexation generates a coloration change of the sol.[15] The corresponding xerogel, however, keeps its transparency. In the case of potassium nitrate, the xerogel SZ10C becomes opaque because of the low solubility of this salt in the sol.

The formation of poly(**6CA**) was never observed with xerogels containing anions other than perchlorate (ClO_4^-). The current is very weak (< 1 μA), the CV response (Fig. 7) is flat (except in the case of sodium oxalate, but the peak intensities are very small) and the characteristic black coloration of polypyrrole does not appear. This study reveals that the presence of ClO_4^- in the xerogel is necessary: this anion, contrarily to the four other tested anions, allows the electropolymerization of **6CA** in the xerogel, a situation that was not obvious.

Discussion of poly(6CA) growth

Influence of the inorganic matrix. The substitution of perchlorate anions in the xerogel by tosylate, salicylate, oxalate or nitrate anions, which are all known doping agents of polypyrrole, prevents the electrochemical formation of poly(**6CA**). However, the absence of ClO_4^- in the xerogel could potentially be compensated by perchlorate anions coming from the electrolytic solution across the inorganic network. But the inability to obtain poly(**6CA**) in a xerogel without ClO_4^- inside reveals that: (1) the xerogel drastically slows down the migration of ClO_4^- coming from the electrolytic solution and (2) the mobility of anions other than ClO_4^- in the xerogel is limited because of steric strains and interactions between the doping species and the inorganic network.

Polymerization rate. The polymerization reaction may be viewed as occurring on an advancing reaction front (of unknown geometry) and when two pyrrole rings are close enough to react, it is likely that neither the coupling reaction itself, nor the electron transfer, are limiting steps. Therefore, polymer growth should occur monolayer by monolayer and be limited by the relative mobility of the pyrrole rings inside the xerogel. As the functionalized pyrrole molecules are entrapped in the xerogel, the current value is probably controlled by the setting up of a quasi-steady state by the advancement of the polymer front into the hybrid material. The polymer growth rate (e) could be estimated (Table 3) on the basis of the passed charge using a few acceptable hypotheses (xerogel density[16] $d = 2$; number of electrons consumed by the electrochemical process,[17] $n = 2.10$) and eqn. (1):

$$e = \frac{Q_{av} M}{(2 + \delta) F t \rho A} \tag{1}$$

where Q_{av} is the average charge deposited during the electrochemical process, M the molecular weight of **6CA** ($M = 195$ g mol^{-1}), δ the doping level of poly(**6CA**) ($\delta = 0.1$), t the duration of the electrolysis, ρ the weight per unit volume of the xerogel ($\rho = 2$ g cm^{-3}), A the area ($A = 1$ cm^2) and F is the Faraday constant (96500 C mol^{-1}).

The calculated values ($0.7 < e < 1.0$ nm s^{-1}) are at least ten times smaller than those of the classically electrogenerated polypyrrole film whose growth is controlled by the pyrrole transport according a quasi-diffusion model. These results are consistant with the hypothesis of a limited mobility, leading to the growth of 1–2 monolayers per second in the composites. From the above considerations, it is possible to evaluate the rate constant of polymerization in the film, on the basis of a bimolecular process, provided some simple straightforward hypotheses, as follows, are made.

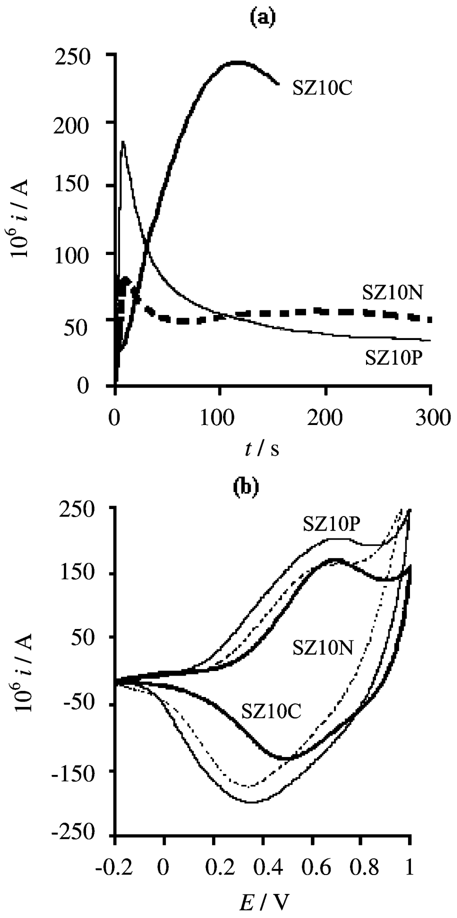

Fig. 5 Influence of the hydrolysis catalyst. (a) Electropolymerization curves $i = f(t)$ and (b) corresponding cyclic voltammetry curves after electropolymerization for **6CA** in the xerogels SZ10C (thick line), SZ10P (thin line) and SZ10N (dashed line). Electropolymerization conditions as for Fig. 1.

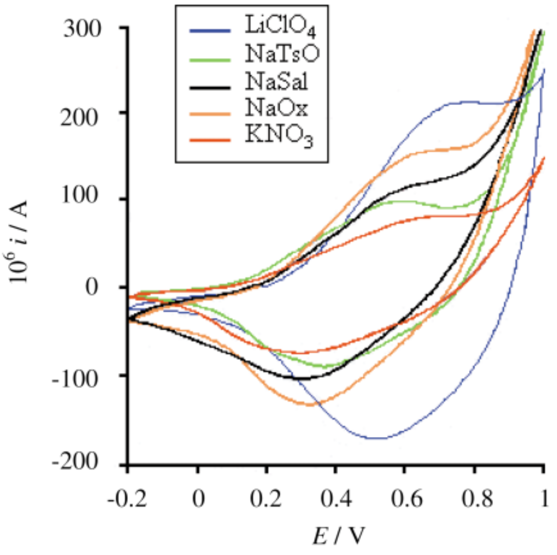

Fig. 6 Influence of the salt in the electrolytic solution. Cyclic voltammetry curves of poly(**6CA**) obtained in the xerogels SZ10C from electrolytic solutions containing 0.1 M LiClO$_4$, NaTsO, NaSal, NaOx or KNO$_3$. Other electropolymerization conditions as for Fig. 1.

From the charge per second used to form the polypyrrole (see above) we can estimate the concentration of polypyrrole formed per unit volume assuming that the reaction occurs in the monolayer adjacent to the previously formed polypyrrole. Although neither the thickness nor the area of this monolayer is known exactly, it may be assumed that the thickness is not very different from 1 nm (the average length of a **6CA** pyrrole) and its surface close to 1 cm^2 (the electrode area). In this case we have: d[polypyrrole]/d$t \approx$ [mole number of polymerized pyrrole units per second]/10^{-10} (mol L^{-1} s^{-1}) $= k(C_{\text{pyrrole}})^2$, k being the polymerization rate constant inside the gel, assuming the well-documented mechanism of cation-radical coupling.[18] The 10^{-10} factor comes from the conversion of units. The concentration of pyrrole rings in the gel is calculated as previously done for other examples, assuming a reasonable approximate value of 2 for the xerogel density. Therefore,

Table 2 Anodic and cathodic peak potentials (respectively E_{p_a} and E_{p_c}) and their difference ΔE ($\Delta E = E_{p_a} - E_{p_c}$) of poly(**6CA**) for various salts in the electrolytic solution

	E_{p_a}/mV	E_{p_c}/mV	ΔE/mV
LiClO$_4$	790	510	280
NaTsO	595	350	245
NaSal	650	285	365
NaOx	685	310	375
KNO$_3$	740	280	460

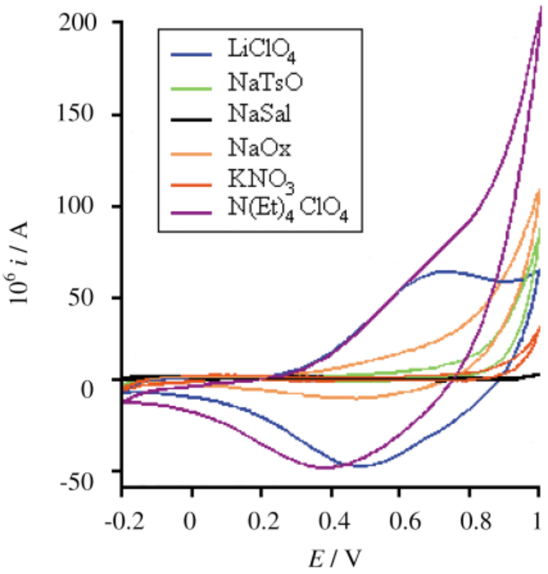

Fig. 7 Influence of the electrolytic salt in the xerogel. Cyclic voltammetry curves of the xerogels SZ10C containing LiClO$_4$, N(Et)$_4$ClO$_4$, NaTsO, NaSal, NaOx or KNO$_3$ after electrolysis. Electropolymerization conditions as for Fig. 1.

Table 3 Growth rate (e) and rate constant (k) calculated from $\Im$, the average charge (Q_{av}) passed in 1 s, and from the concentration of monomers in 6CAwac and SZ10C xerogels. 6CAwac is a xerogel containing **6CA** and LiClO$_4$ whose inorganic part is composed only of zirconium oxopolymers (see ref. 6)

	6CAwac	SZ10C
$\Im$/μA or μC s^{-1a}	150	200
e/nm s^{-1b}	0.7	1.0
c/mol L^{-1}	3.6	0.5
k/L mol^{-1} s^{-1c}	0.6	40

[a] $\Im = \frac{Q_{\text{av}}}{t}$. [b] From eqn. (1). [c] From eqn. (2).

the k values (Table 3) are comprised between 0.6 and 40 L mol^{-1} s^{-1}, as calculated from eqn. (2):

$$k = \frac{Q_{\mathrm{av}}}{(2+\delta)FtVc^2} \tag{2}$$

where Q_{av}, δ, t and F are as above, V is the volume ($V = 10^{-10}$ L) and c the concentration of **6CA** in the xerogel.

However, the polymerization of **6CA** seems to be easier in the mixed silicon–zirconium oxopolymer xerogel than in the pure zirconium oxopolymer xerogels since the k value is higher. These values are extremely low when compared to the 10^8 value estimated in an acetonitrile solution.[19] However, the ratio of 10^8–10^9 is to be compared, for example, to the ratio of the diffusion between a classical liquid and a solid phase such as an oxide, since they have the same origin in the restriction of molecular motion; the same difference in the orders of magnitude are encountered.[20]

Conclusion

This study confirms the results obtained in a previous work: the electrochemical synthesis of poly(**6CA**) is possible in a xerogel. The electrochemical formation of the organic polymer requires the presence of ClO_4^- in the xerogel, which seems to be unavoidable.

Moreover, the combination of oxopolymers of silicon and of zirconium is profitable because the SZ10C and SZ12C xerogels exhibit better features than the xerogels whose inorganic matrix is only constituted by zirconium oxopolymers. Indeed, the formation of poly(**6CA**) with good characteristics is easier in SZ10C and SZ12C. The adherence of the hybrid material onto ITO electrodes is excellent and no morphological defect appears during the electrochemical step. This method is therefore efficient to prepare conducting polymer based hybrid materials.

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