

# Functionalization of polypyrroles with acids and $\beta$ -diketones as complexing groups. Part 2:† electrochemical growth of polypyrrole into hybrid zirconium oxopolymer sol/gel coatings

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New hybrid materials were prepared by a sol-gel route from zirconium propoxide and functionalized polypyrroles bearing a complexing group (carboxylic acid or  $\beta$ -diketone). Formation of polypyrroles in the gel deposited on an indium tin oxide (ITO) electrode was performed electrochemically in aqueous media. The optimal conditions for the preparation of stable sols were determined, as well as the deposition conditions to obtain reproducible transparent uniform coatings in which electropolymerization was possible. The xerogels as well as the composites after polymerization were analyzed with the help of optical microscopy (OM), scanning electron microscopy (SEM) and X-ray fluorescence. The electrochemical characteristics of the composites were investigated by cyclic voltammetry and their adherence evaluated. From the polymerization rate and simple assumptions, the rate constant for pyrrole polymerization inside the gels has been evaluated.

The preparation of composite materials from conducting polymers and inorganic coatings is a recent challenge, because it allows the chemical resistance of inorganic sol-gel polymers and the electronic properties of conjugated polymers to be allied in the same material.<sup>1,2</sup> The main procedures to prepare composites of conductive polymers and inorganic materials have been described: (1) impregnation of a porous inorganic network by conducting polymer precursors,<sup>3,4</sup> followed by chemical oxidation into the conducting polymer inside the inorganic matrix (a conducting polymer suspension was used in a slightly different case<sup>5</sup>). (2) Chemical polymerization of aniline or pyrrole in the presence or absence of a chemical oxidant, on transition metal oxide microparticles.<sup>6–9</sup> (3) Chemical or electrochemical polymerization of silanized organic monomers into a preformed inorganic silica gel<sup>10,11</sup> or electrochemical polymerization in the precursor silica sol.<sup>12,13</sup> However, the analogous route of composite preparation through the sol-gel approach has not, to our knowledge, been extended to transition metal oxides or oxopolymers, which is unexpected given the various physicochemical properties of these compounds. The reason is probably that the sol-gel polymerization of transition metal alkoxides is more tedious, requiring well-defined conditions in order to avoid the obtention of precipitates or stable sols.<sup>2,14</sup>

It is also well-known that a condensation controlling agent is almost always necessary in the sol-gel polymerization of transition metal alkoxides,<sup>15</sup> due to the high reactivity of the latter when compared to silicon analogs. The first and most widely used polymerization controller is protons,<sup>16</sup> but organic complexing agents may also be efficient.<sup>17</sup> However, their use has been much less investigated, although this

research field is rapidly expanding. The copolymerization of zirconium or titanium alkoxides and silicon alkoxides has also been investigated and is rapidly emerging as a new research domain.<sup>18</sup>

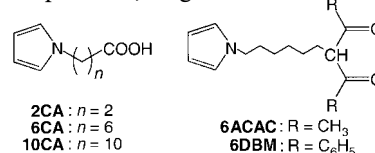
We have chosen to investigate the preparation of polypyrrole-zirconium oxopolymer composite coatings, using first the sol-gel polymerization process to prepare hybrid coatings, and then *in situ* electropolymerization to yield the conducting polymer. For this goal, we have prepared a series of molecules having the pyrrole ring at one end, while the other end is made of a specific zirconium complexing agent, allowing its use both as a controlling agent for the sol-gel process and as the precursor of the conducting polymer.

We have prepared and described pyrrole monomers bearing pendant groups functionalized by either an acetylacetonate (ACAC), a dibenzoylmethane (DBM) or a carboxylic (CA) moiety (Scheme 1), which are classically known as good ion complexing groups. The classical electropolymerization of these functionalized pyrroles and the electrochemical properties of the polymers are described in the accompanying paper.<sup>19</sup>

## Experimental

### Syntheses of the sols and gels

In a typical experiment, a given amount of functionalized



Scheme 1 CA and  $\beta$ -diketone functionalized pyrroles.

pyrrole is dissolved in dry propanol, with a variable proportion (which can be zero) of acetic acid added. To this solution is added a given amount of zirconium propoxide (70% solution in propanol, Aldrich), and finally a given amount of water (in the form of 10% aqueous ethanol). The sol is allowed to react for 1 h, and then it is dip-coated (or applied with a pencil brush) onto indium tin oxide (ITO) plates where it is allowed to gel; afterwards a low temperature treatment (75–85 °C overnight under reduced pressure) converts the gels into xerogels. In some cases lithium perchlorate is added to the sol ( $[\text{LiClO}_4]_{\text{sol}} = 0.1 \text{ mol L}^{-1}$ ) before coating, in order to favor the electropolymerization.

### Electrochemical set-up

Polymerization experiments were performed in a one-compartment cell fitted with a saturated calomel reference, a platinum counter electrode with a  $5 \text{ cm}^2$  area and for the working electrode an ITO coated electrode prepared as above (area:  $1 \text{ cm}^2$ ). The electrochemical apparatus was a PGZ 301 Potentiostat (Radiometer) monitored by a personal computer using Voltamaster 4 electrochemical software. All potentials are referenced to a saturated calomel electrode (SCE). The films were prepared at a constant potential of +1080 mV. The solvent was distilled water, with  $0.1 \text{ mol L}^{-1}$  lithium perchlorate as the electrolyte salt. However, the electrochemical cycling of the films was carried out in acetonitrile containing  $0.1 \text{ mol L}^{-1} \text{ LiClO}_4$  at a scan rate of  $50 \text{ mV s}^{-1}$ . The charge used to form the films was determined by integration of the polymerization currents.

### Film characterization

In addition to electrochemical cycling, the films were characterized by optical microscopy (Zeiss Axiotech with a CCD Sony DXC-107AP camera) before and after polymerization, X-ray fluorescence (Fischerscope Xray 1600) before and after polymerization and scanning electron microscopy (SEM) for selected samples. Adherence tests were performed with a calibrated adhesive tape according to the French standard T30-038. The adherence was estimated on a 0 to 5 level, 0 corresponding to an excellent adhesion (no deposit present on the tape, even after incisions of the coating) and 5 corresponding to poor adhesion (more than 50% of the coating remains on the tape after the test).

## Results and discussion

### Gel preparation and analysis

**CA pyrroles.** The preparation of stable zirconium alkoxide sols requires controlled amounts of polymerization inhibitors. The functionalized monomers all act as gelification controllers, since carboxylic acids as well as  $\beta$ -diketones are known to be efficient towards this goal.<sup>2</sup> Therefore, the functionalized pyrrole plays the double role of sol-gel polymerization controller and precursor of the conducting polymer in the composite. The initial composition of the sol has to be carefully determined, because the polymerization of transition metal alkoxides is very sensitive to experimental conditions upon coating and further drying on a substrate. In order to determine the best conditions for the sol-gel polymerization, acetic acid (AcOH) was used as a model compound.

**Gelification conditions.** We have determined the best conditions for the preparation of stable sols, which turn into stiff xerogels in the presence of acetic acid as an inhibitor and water. Fig. 1 summarizes the sol-gel state diagram according to the amount of acetic acid (AcOH) and water added for the polymerization. Stable sols are obtained when the AcOH content exceeds 2, which is as expected, since this corresponds to at least a six-fold coordination of the zirconium. It is known that zirconium species in which the coordination number of Zr is higher than 5 condense slowly.<sup>18</sup> As often

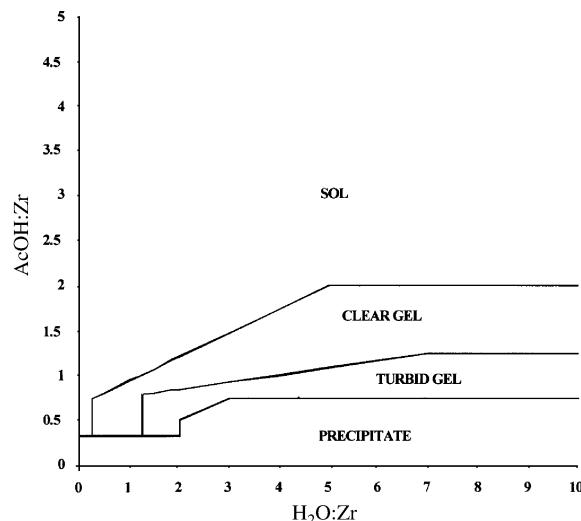


Fig. 1 Sol-gel state diagram of  $\text{Zr}(\text{OPr})_4\text{-AcOH-H}_2\text{O}$ ; solvent propanol.

when dealing with transition metal alkoxides, the relative water content is less important than the inhibitor proportion in the medium, although the latter plays a role in the course of the electropolymerization. However, when the sol is cast on planar substrates and heated, simultaneous departure of AcOH and condensation occurs, which causes the formation of a gel and subsequent xerogel.

In the case of CA pyrroles, the complexing power of the functionalized pyrrole is lower than that of acetic acid, and the use of the functionalized pyrrole alone leads to precipitates upon water addition. The complexing power of the CA pyrrole has been tested only for a complexant : Zr ratio equal to 4. In this case, precipitation occurs with **2CA** after addition of more than 0.5 equiv. water, 0.125 equiv. in the case of **6CA** and almost instantaneously in the case of **10CA**, which allows us to order the complexing power of the CA pyrrole: **2CA** > **6CA** > **10CA**, as might be expected from the steric hindrance of the alkyl chain present. Clear transparent xerogels can be obtained using pure **2CA** and **6CA**; however, electropolymerization always failed under these conditions with **2CA**.

Since there is only a restricted region where appropriate sols and gels are obtained, AcOH was therefore frequently used as an auxiliary polymerizing agent. It is clear from the sol-gel polymerization diagram that stable sols are obtained when more than 2 equiv. of acid per zirconium are used. In fact, the use of excess acetic acid does not seem to have a strong influence on the xerogel, since the acid is eliminated in the drying phase during the gel to xerogel conversion. Therefore, the composites were prepared mainly using two functionalized pyrroles, **2CA** and **6CA**, due to the weak complexing power of **10CA**, which limited its use for preparing hybrid materials.

**Preparation of the functionalized xerogels.** Two conditions were tested for the xerogel synthesis, either hydrolysis with a certain amount of water included or hydrolysis effected by atmospheric water during the drying process.

Table 1 describes the properties of gels prepared with **6CA** before and after electropolymerization, as a function of the proportion of both functionalized pyrrole and AcOH included. As can be seen, the addition of large quantities of AcOH leads to films with good mechanical properties, but competition between complexation of AcOH and **6CA** on zirconium occurs probably in favor of the former, and thus is detrimental to our aim. Finally, the proportions of functionalized pyrrole given in Table 1 appeared to be the best conditions, both for gelification and the subsequent electropolymerization to form the composite.

**Table 1** Summary of the characteristics of the xerogels prepared from **6CA** before and after electropolymerization of different sols. *A* gives an indication of the adherence of the coatings

Type <sup>a</sup>	Composition			Gel appearance after deposition	<i>A</i>	Gel after electropolymerization	<i>A</i>
	<b>6CA</b> : Zr	AcOH : Zr	H <sub>2</sub> O : Zr				
6CAac1	2.35	0.3	0	Transparent uniform	1	No apparent polymer formation; weak electrooxidation current	2
6CAac2	2.35	3.5	0	Transparent uniform	2	Black uniform polymer layer 130 < <i>I</i> <sub>max</sub> < 250 μA	2
6CAwac1	3.55	14.3	78	Transparent uniform	2	Black uniform polymer layer 250 < <i>I</i> <sub>max</sub> < 300 μA	2
6CAw1	3.8	0	0.125	Transparent uniform	1	Black polymer layer in large scales 70 < <i>I</i> <sub>max</sub> < 150 μA	1
6CAw2	3.8	0	0.025	Transparent uniform	2	Black scales with cracks in the gel layer 80 < <i>I</i> <sub>max</sub> < 140 μA	4

<sup>a</sup> In the gel nomenclature, **6CA** stands for gels prepared from **6CA** functionalized pyrrole, ac and w stand for acetic acid or water added for the sol-gel polymerization, respectively (the quantities used are given in the composition entries), while the last digit qualifies the gel for further referencing (OM and SEM pictures).

The gelification conditions for **2CA** did not make an appreciable difference with **6CA**, the best mechanical properties also compatible with the electropolymerization process for the gels being obtained by using either 3 equiv. **2CA**, 2.5 equiv. AcOH, without added water or 3.5 equiv. **2CA**, 10 equiv. AcOH and a large excess of water (70 equiv.). The adherence of the gels is around 1 to 2 in such cases.

**6ACAC pyrrole.** The gelification diagram of zirconium propoxide in the presence of ACAC was previously determined by us.<sup>20</sup> As before, it represents a good model for the sol-gel condensation in the presence of our ACAC functionalized pyrrole, **6ACAC**. As previously stated, **6ACAC** could either be used alone or in addition with ACAC. However, the complexing power of the acetylacetone group is higher than that of the carboxylic group, so that lower amounts of complexant were needed. For the same reason, problems linked to the weakening of the complexing power of the substituted complexants were not encountered in this case, so that **6ACAC** was mainly used alone. In fact, in a few trials made with added ACAC the deposits remained very soft and often sticky, showing that the xerogel state could not be reached under a low (100 °C) thermal treatment, while higher temperatures could have harmed the functionalized pyrrole and cracked the coating. Since a proportion of complexing agent above 0.6 was required in order to obtain stable sols, two proportions of

**6ACAC** were tried for the composite preparation, 1 and 3 equiv. (relative to the Zr molarity). The results are summarized in Table 2. It should be remarked that with 3 equiv. of **6ACAC**, the resulting xerogels are very often relatively soft. On the contrary, with only 1 equiv. of complexing agent, stiff to hard xerogels can be obtained, but excess water is needed. The adherence of the corresponding gels is 2.

A few trials were also made with **6DBM**, but, although an orange transparent hard gel could be obtained with *ca.* 3 equiv. of **6DBM** and 3 equiv. of additional ACAC, the subsequent electropolymerization was completely unsuccessful and investigations on this ligand were not pursued.

**Influence of electrolyte addition on the gelification.** In almost all cases investigated, we have checked the influence of the addition of an electrolyte salt, since this had proved in several cases to be important for the electropolymerization. LiClO<sub>4</sub> has been chosen as the electrolyte salt, since is often used for pyrrole electropolymerization. In most cases this has little influence on the gelification process and on the resulting properties of the gels and xerogels. Sometimes the transparency of the xerogels changes upon salt addition, and in rare cases, the xerogels present cracks, but such occurrences are exceptional and apparently restricted to the cases where relatively large amounts of salt are added (when [LiClO<sub>4</sub>] > 0.5 mol L<sup>-1</sup> in the corresponding sol).

**Table 2** Summary of the characteristics of the xerogels prepared from **6ACAC** before and after electropolymerization of different sols

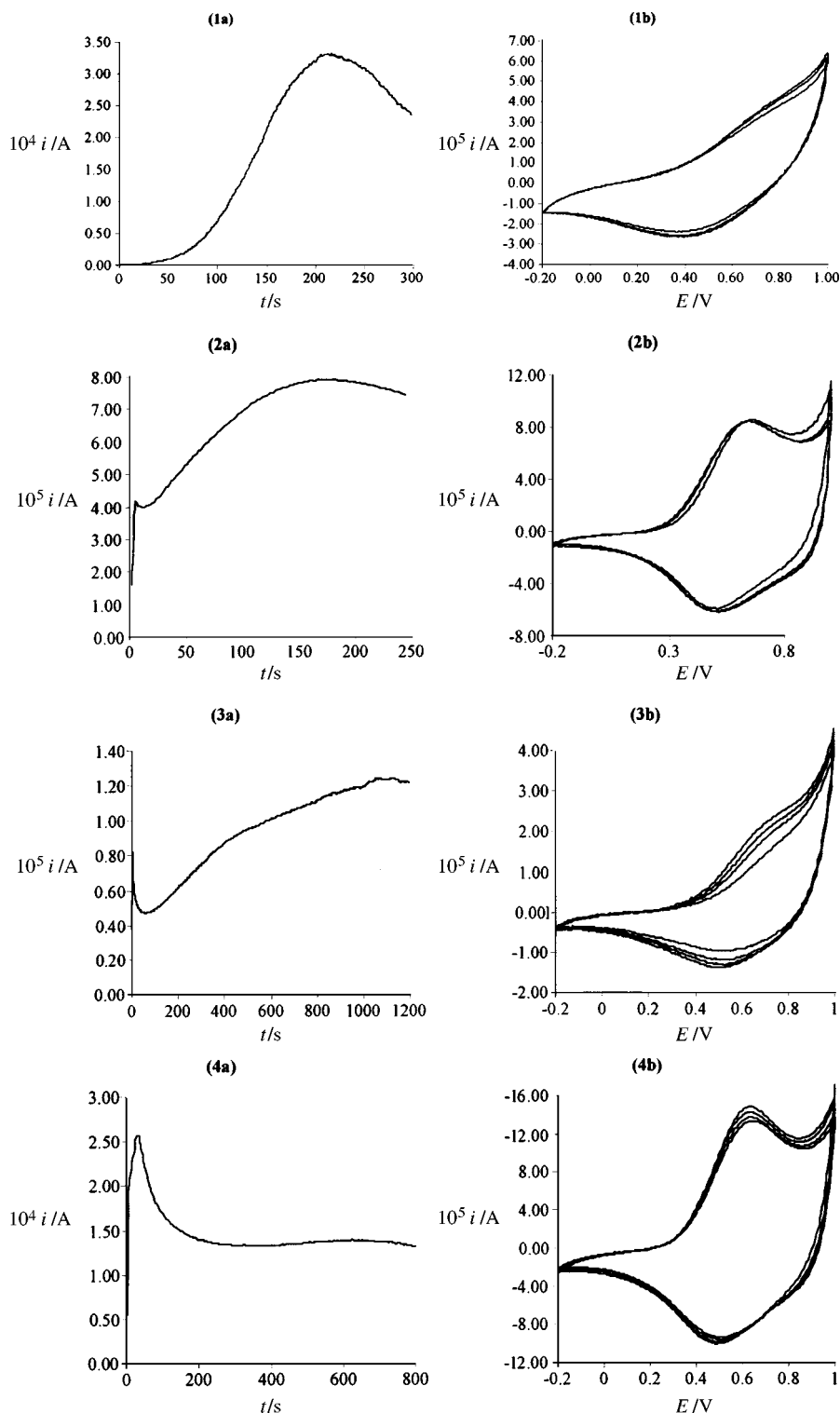
Type <sup>a</sup>	Composition			Gel appearance after deposition	Gel appearance after electropolymerization	
	<b>6ACAC</b> : Zr	Acac : Zr	H <sub>2</sub> O : Zr		Without LiClO <sub>4</sub>	With LiClO <sub>4</sub>
6ACAC + 1	3	3	0.5	Soft sticky orange gel	Light black film <i>I</i> constant <i>ca.</i> 35 μA	Uniform deep black film <i>I</i> <sub>max</sub> ~ 650 μA
6ACAC + 2	1.5	1.5	0.5	Transparent soft gel	—	Uniform deep black film 60 < <i>I</i> <sub>max</sub> < 130 μA
6ACAC1	3	0	0.5	Transparent soft gel	Black films with scales 200 < <i>I</i> <sub>max</sub> < 300 μA	Uniform deep black film 250 < <i>I</i> <sub>max</sub> < 400 μA
6ACAC2	3	0	1	Soft sticky orange gel	—	Uniform black films 200 < <i>I</i> <sub>max</sub> < 300 μA
6ACAC3	3	0	3	Stiff transparent gel	Uniform deep black film <i>I</i> <sub>max</sub> <i>ca.</i> 250 μA followed by a plateau ( <i>ca.</i> 150 μA).	Black films with scales 300 < <i>I</i> <sub>max</sub> < 400 μA
6ACAC4	1	0	0.5	Hard transparent gel	Black films with scales 200 < <i>I</i> <sub>max</sub> < 300 μA	Uniform deep black film <i>I</i> <sub>max</sub> <i>ca.</i> 800 μA
6ACAC5	1	0	5	Hard transparent gel with scattered cracks	Uniform light grey film <i>I</i> <sub>max</sub> <i>ca.</i> 3 μA	Uniform deep grey film <i>I</i> <sub>max</sub> <i>ca.</i> 75 μA

<sup>a</sup> In the gel nomenclature, **6ACAC** stands for gels prepared from **6ACAC** functionalized pyrrole, ac and w stand for acetic acid or water added for the sol-gel polymerization, respectively (the quantities used are given in the composition entries), + indicates additional acetylacetone, while the last digit qualifies the gel for further referencing (OM and SEM pictures).

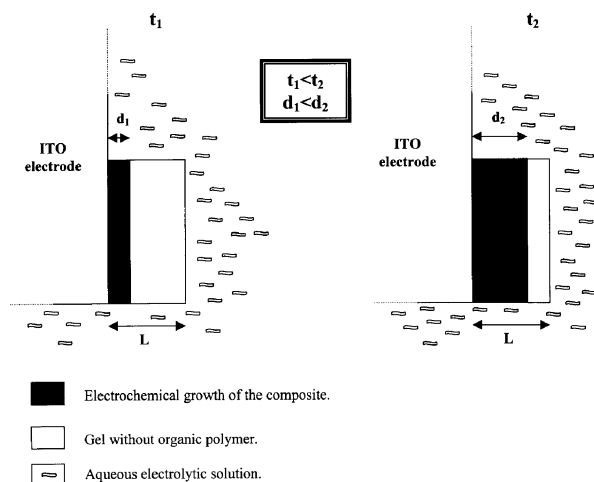
**Electropolymerization reaction and electrochemical characteristics of the composites.** *General behavior.* After the gelification-drying process, the gels were submitted to electropolymerization by constant potential electrolysis in an aqueous electrolyte. It is not obvious that a homogeneously polymerized layer can be obtained through such a process, because of the restricted mobility of the pyrrole moieties

inside the gel and problems linked to the gel porosity. In some cases no polymerization was observed, in some cases partial polymerization, and in a few cases, homogeneous polymerization in the xerogel layer, leading to an intrinsic composite. The efficiency of the electropolymerization is indicated in both Table 1 and 2. In all cases, the electropolymerization curves were registered as well as the cyclic voltammograms of the resulting polymers.

Fig. 2 shows both types of curves for the **2CA**, **6CA**, **10CA**



**Fig. 2** (a) Electropolymerization curves  $i = f(t)$  and (b) corresponding cyclic voltammetry curves after electropolymerization of (1) 2CAwac, (2) 6CAw1, (3) 10CAwac1 and (4) 6ACAC2. Electropolymerization of functionalized pyrrole in ITO electrode-deposited xerogels was performed in aqueous solution containing  $0.1 \text{ mol L}^{-1} \text{ LiClO}_4$  at 1080 mV. Cyclic voltammetry experiments were carried out in acetonitrile solution containing  $0.1 \text{ mol L}^{-1} \text{ LiClO}_4$  between  $-200$  and  $1000 \text{ mV}$  with a potential sweep rate of  $50 \text{ mV s}^{-1}$ .



**Scheme 2** Schematic representation of the growth of the composite in the coating:  $t_1$  and  $t_2$  are the electrolysis times,  $d_1$  and  $d_2$  the thicknesses of the electropolymerized composite and  $L$  the gel layer thickness.

and **6ACAC** based xerogels. It is clear that in all cases but **2CA** quasi-steady state currents are obtained for the polymerization process, with values approximately in the range  $1\text{--}4 \times 10^{-4} \text{ A cm}^{-2}$ , except for **10CA**, whose polymerization is rather more difficult, as confirmed by the characteristics of the gels obtained. With **2CA**, the current displays a relatively long induction period, followed by a maximum ( $150 < I_{\text{max}} < 400 \mu\text{A}$ ); however, this induction period may be due to problems linked to electrolyte diffusion inside the gel coating. Since the pyrroles are immobilized inside the xerogel, after the establishment of the steady state the current value is probably kinetically controlled by the advancement of the polymer front inside the composite (Scheme 2). This hypothesis had been previously proposed and analyzed in the case of the transient currents observed in the course of pyrrole polymerization inside Nafion gels,<sup>21</sup> a case that resembles the present one (although the Nafion gel internal structure also plays a particular role in the electropolymerization process). From the current values, we observe that the rate of growth of the polymer film throughout the composite is about  $100 \mu\text{C s}^{-1}$  for **6CA** and **2CA** and  $250 \mu\text{C s}^{-1}$  for **6ACAC**, which correspond to a thickness increase of 0.5 and 1.3 nm per second, respectively, in the composite.<sup>22</sup> These values are about ten times smaller than in an unstirred solution, where the growth of the films is controlled by the transport mode of pyrrole through a quasi-diffusion process (for a  $0.01 \text{ mol L}^{-1}$  concentration of functionalized pyrrole, a current of about 1 mA is obtained). In our case, this mechanism is in good agreement with the hypothesis of restricted mobility of the pyrrole in the films, leading to the growth of 1–2 monolayers in the composites per second. From the above results, it is possible to evaluate the rate constant of polymerization in the film, on the basis of a bimolecular process, and with some simple assumptions.

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 after monolayer and be limited by the relative mobility of the pyrrole rings inside the xerogel. From the charge per second (see above) used to form the polypyrrole we can estimate the concentration of polypyrrole formed per volume unit, assuming that the reaction occurs in the monolayer adjacent to the previously formed polypyrrole. Although neither the thickness nor the area of this monolayer are known exactly it can be assumed that the thickness is not very

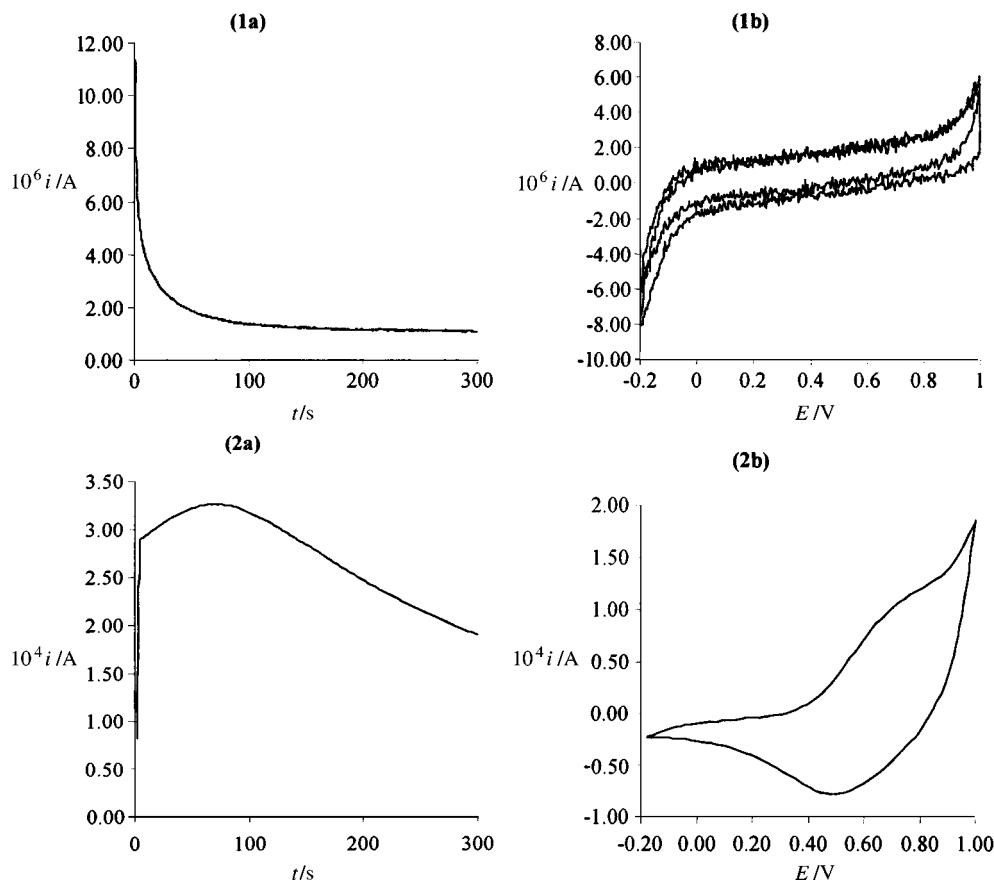
different from 1 nm (the average length of a **6CA** pyrrole) and its surface close to  $1 \text{ cm}^2$  (the electrode area).

With these assumptions we obtain:  $d[\text{polypyrrole}]/dt \approx [\text{mol of polymerized pyrrole units per second}]/10^{-10} (\text{mol L}^{-1} \text{ s}^{-1}) = k(C_{\text{pyrrole}})^2$ ,  $k$  being the polymerization rate constant inside the gel, assuming the well-documented mechanism of cation–radical coupling.<sup>23</sup> The concentration of pyrrole rings in the gel is calculated to be as previously, assuming a reasonable value of 2 for the xerogel density.<sup>24</sup> Therefore, the  $k$  values are *ca.*  $0.1 \text{ L mol}^{-1} \text{ s}^{-1}$  for **6CA** and  $1.5 \text{ L mol}^{-1} \text{ s}^{-1}$  for **6ACAC**. These values are extremely low when compared to the  $10^8 \text{ L mol}^{-1} \text{ s}^{-1}$  value estimated in an acetonitrile solution.<sup>25</sup> However, the ratio of  $10^8\text{--}10^9$  for the rate constants must be compared to the ratio of the diffusion in a classical liquid and in 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 is encountered.<sup>26</sup>

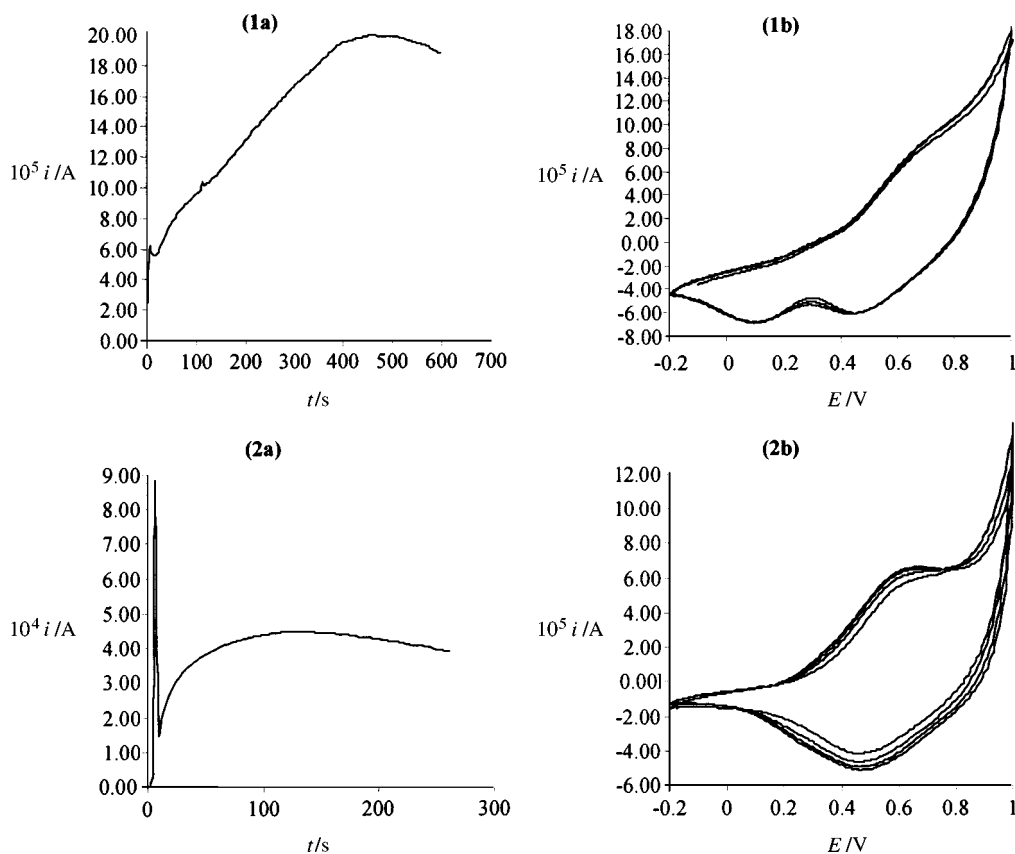
In the cyclic voltammetry the potential values are quite similar to these observed in solution (acetonitrile<sup>18</sup>), which shows that good quality functionalized polypyrroles are formed in all cases. In addition, for CA pyrroles, no splitting of the peaks is observed, in contrast to what may sometimes happen in solution, tending to show that in the gels there is limited mechanical relaxation during the cycling, as might be expected from functionalized zirconium oxopolymers.

*Influence of electrolyte salt present in the xerogel.* In contrast to the sol–gel process, the presence of lithium perchlorate strongly affects the course of the polymerization reaction, but in a different way depending on the functionalized pyrrole precursor of the xerogel. We have found that **6CA** and **2CA** display completely opposite behaviors. On the one hand the presence of electrolyte salt was necessary to electropolymerize **6CA** inside the gels. On the other hand, not only was **2CA** easily polymerized without added salt, but besides, salt addition was always harmful to the efficiency of the electropolymerization reaction. For example, Fig. 3 shows the polymerization currents and cyclic voltammograms obtained from **6CA** xerogels identical in every respect except for the presence of added lithium perchlorate. It is clear that here the presence of the electrolyte salt in the xerogels favors the electropolymerization reaction. Regardless of the fact that its polymerization is significantly less efficient, **10CA** appears to display behavior analogous to **6CA**. Polymerization currents appear to be slightly higher in the case of **2CA** (without  $\text{LiClO}_4$  in the xerogel,  $150 < I_{\text{max}} < 400 \mu\text{A}$ ) compared to **6CA** (with  $\text{LiClO}_4$  added,  $70 < I_{\text{max}} < 300 \mu\text{A}$ ). On the other hand, CV currents are lower for **2CA** (Fig. 2). Finally, in the case of **6ACAC**, the polymerization seems to occur whether or not electrolyte salt is present in the xerogel. However, the cyclic voltammograms are different, as pictured in Fig. 4. Although the observed splitting of the reduction peak (when there is no  $\text{LiClO}_4$  in the gel) is difficult to explain, the main difference between both cases would be the higher resistivity of the films prepared in the absence of electrolyte, as shown by the increased difference between the anodic and cathodic peak potentials (with  $\text{LiClO}_4$  in the xerogel:  $\Delta E_p = 200 \text{ mV}$ ; without  $\text{LiClO}_4$ :  $\Delta E_p = 325 \text{ mV}$ ).

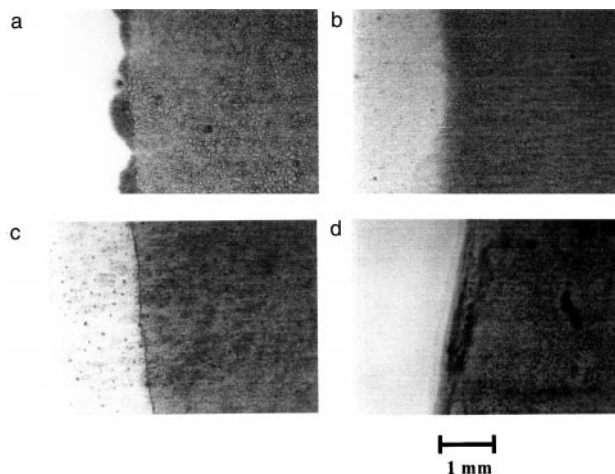
It is difficult to completely explain this situation, but, since the salt is necessary for the polymerization of **6CA** and **10CA** it is clear that the compactness of the xerogels prevents the diffusion of the electrolyte salt from the solution into the xerogel, while this is not the case with **2CA**. Indeed, the electropolymerization of **2CA** can be performed in  $\text{LiClO}_4$ -free xerogel. Nevertheless, a rather long induction time is observed, presumably because the diffusion of  $\text{LiClO}_4$  (from the electrolytic solution) through the coating is not instantaneous. The situation for **6ACAC** gels should be in between, with the electrolyte salt not having such an important effect as in the case of the CA-based xerogels. This is probably the



**Fig. 3** (a) Electropolymerization curves  $i = f(t)$  and (b) corresponding cyclic voltammetry curves after electropolymerization of 6CAwac1 (1) without  $\text{LiClO}_4$  and (2) with  $0.1 \text{ mol L}^{-1} \text{ LiClO}_4$  in the corresponding sol. Electropolymerization conditions as for Fig. 2.



**Fig. 4** (a) Electropolymerization curves  $i = f(t)$  and (b) corresponding cyclic voltammetry curves after electropolymerization of 6ACAC3 (1) without  $\text{LiClO}_4$  and (2) with  $0.1 \text{ mol L}^{-1} \text{ LiClO}_4$  in the corresponding sol. Electropolymerization conditions as for Fig. 2.



**Fig. 5** Optical micrographs (magnification  $\times 50$ ) after electro-polymerization of a coating of: (a) 2CAwac1, (b) 6CAwac1 with  $0.1 \text{ mol L}^{-1} \text{ LiClO}_4$  added to the sol, (c) 6CAac2 with  $0.1 \text{ mol L}^{-1} \text{ LiClO}_4$  added in the sol and (d) 6ACAC + 1 with  $0.1 \text{ mol L}^{-1} \text{ LiClO}_4$  added in the sol. The light-colored zone at the left of each micrograph represents the part of the coating that was not immersed in the electrolytic solution whereas the dark zone at the right corresponds to the part of the coating immersed in the electrolytic solution.

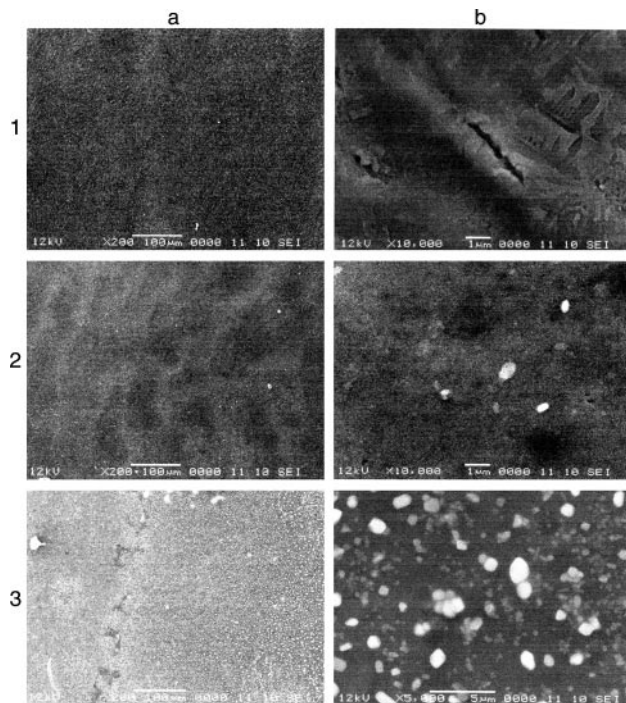
result of the higher porosity of the xerogels made with ACAC type complexants, which has been demonstrated previously.<sup>27</sup>

**Characterization of the composites.** The deposits of the composites have been characterized both by optical microscopy (OM), scanning electron microscopy (SEM) and X-ray fluorescence. The X-ray fluorescence is in our case only sensitive to the zirconium content as well as the tin and indium content of the conductive part of the ITO electrode on which the film is deposited. Although this technique is of limited use in our case, we have used this method to check that the ratio of Zr in the gels to the Sn in the electrode material did not vary before and after the electropolymerization; 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 sol-gel chemistry with our type of gels.

Typical optical micrographs of the gels after electropolymerization are given in Fig. 5. It is clear again that the polymerization reaction does not destroy the xerogel, and that a uniform black conductive composite layer can be formed. The pictures allow one to distinguish between the electropolymerized gel (black) and the unpolymerized part (white, not dipped in the electrolyte), which displays no change compared to its appearance before the electropolymerization. The SEM pictures of the films, for three different types of gels, are presented in Fig. 6. It is clear that the 6CA gels are very homogeneous, although some very small cracks are discernable when a relatively high content of both water and acetic acid are used, whereas the gels polymerized without water or acetic acid remain completely uniform and crackless below the  $\mu\text{m}$  scale. The ACAC gels, which also look very homogeneous when observed at a low magnification, show very small zirconium oxopolymer aggregates homogeneously distributed on the coating. This confirms what has been previously observed in the case of gels issued from the condensation of zirconium alkoxides in the presence of diketonic bidentate ligands.<sup>27</sup>

## Conclusion

We have presented the preparation and properties of some new zirconium oxopolymer-polypyrrole composites through successive sol-gel deposition and electropolymerization.



**Fig. 6** SEM micrographs [magnification (a)  $\times 200$  and (b)  $\times 10000$  except (3b)  $\times 5000$ ] after electropolymerization of different coatings: (1) 6CAwac1, (2) 6CAac2 and (3) 6ACAC2. All sols used to deposit the corresponding coating on the ITO contained  $0.1 \text{ mol L}^{-1} \text{ LiClO}_4$ . Electron energy: 12 keV. The coatings were not metallized.

Several functionalized pyrroles have been tested and pyrroles bearing an acetylacetone (6ACAC) or a carboxylic moiety linked through a six-carbon chain (6CA) have been found to be the best candidates for the preparation of both good quality xerogels and the subsequent electropolymerization of functionalized pyrrole into polypyrrole in the xerogels; the best conditions for obtaining hard and uniform coatings have been determined. It should be emphasized that the polymerization reaction has been conducted in water, which is not commonly encountered in functionalized pyrrole electrochemistry (often due to their low solubility in water<sup>28</sup>), and which therefore significantly enlarges the range of potential applications for this new process. These materials are currently being investigated for corrosion protection.

## References and notes

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