# ARTICLES

## Hybrid Material Polypyrrole/[SiCr(H₂O)W₁₁O₃₉]⁵⁻: Electrogeneration, Properties, and Stability under Cycling

**Hybrid Material Polypyrrole/$[SiCr(H_2O)W_{11}O_{39}]^{5-}$: Electrogeneration, Properties, and Stability under Cycling**

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Hybrid materials constituted by polypyrrole doped with the polyoxometalate (POM) anion [SiCr(H₂O)W₁₁O₃₉]⁵⁻ were electrogenerated from acetonitrile solutions. The electrochemical behavior of the hybrid films was studied by cyclic voltammetry in three different electrolytes formed by two anions and two cations, dissolved in acetonitrile. Following both, the film weight evolution and the solutions composition with cycling, together with an EDX study of the film showing the electrochemical evolution, have allowed the identification of the ions interchanged during the redox processes for the different studied electrolytes. Prevalent cation interchange, continuous substitution of the POM anion by the anion in solution, and partial electrodissolution of the hybrid film were identified as prevalent processes in the different electrolytes. Conducting measurements show that the films present a high room temperature conductivity that is thermally activated. Magnetic measurements confirmed the presence of the paramagnetic POM in the films and indicate that the number of pyrrole monomers per cationic charge is about 4.5. These results have been confirmed by elemental analysis.

## 1. Introduction

Hybrid films made of polypyrrole (Ppy) (Figure 1a) and polyoxometalates (POMs) (Figure 1b) have been attracting much interest in electrochemistry and catalysis due to their easy generation and good electrocatalytic and electrochemical properties.[1−4] Keggin-type polyoxometalates inserted into a Ppy matrix confer these materials special electrocatalytic,[5−10] photoelectrochemical,[6,11] and electrochemical[3,12] properties that make them very useful as catalysts.[2,13]

The most used POMs are the Keggin heteropolyanions of formula $[X^{n+}M_{12}O_{40}]^{(8-n)-}$ (M = $W^{VI}$ or $Mo^{VI}$) (Figure 1b). One of the advantages of this highly symmetric structure is the possibility of substitution of one or more of the constituents M(VI) ions by transition metals ions (addenda), like W(VI), Mo(VI), V(V), and Re(VII), and by many other of the first row, such as Cr(III), Mn(II), Fe(III), Co(III), Co(II), and Cu(II), although for these last cases the terminal oxo group is replaced by a water molecule.[14] In this way, the electrochemical character of the POMs can be widely changed. For example, in the reduction of $[PW_{11}^{VI}Mo^{VI}O_{40}]^{3-}$ and of $[PW_{11}^{VI}V^{V}O_{40}]^{4-}$ the added electron is accepted by the Mo and V atoms, respectively, forming $[PW_{11}^{VI}Mo^{V}O_{40}]^{4-}$ and $[PW_{11}^{VI}V^{IV}O_{40}]^{5-}$ These sub-
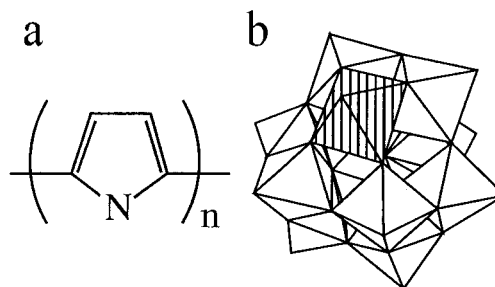


**Figure 1.** Polypyrrole (a) and the Keggin polyoxometalate [SiCr-(H₂O)W₁₁O₃₉]⁵⁻ used in this work (b). The Cr³⁺ ion is located in the shaded octahedron.

stituted POM complexes have been widely used as heterogeneous catalysts.[15] Polymer doped with these substituted POM ions are much more interesting because they exhibit the redox properties inherent to both the POMs and the polymer moiety.[5,16] Bidan and co-workers reported the synthesis of poly(*N*-methylpyrrole) films doped with the iron-substituted heteropolytungstate [PFe^{III}(H₂O)W₁₁O₃₉]⁴⁻ and its electrochemical properties in solution in the presence of NO₂⁻ ions.[17] Polyaniline films doped with H₄[PFe^{III}(H₂O)Mo₁₁O₃₉] and H₄[PMn^{II}(H₂O)-Mo₁₁O₃₉] were described by Lapkowski et al.[13] Wang et al. described polyaniline films doped with [PV₂Mo₁₀O₄₀]⁵⁻ formed on carbon fiber microelectrodes and its utilization for the electrocatalytic reduction of ClO₃⁻ and BrO₃⁻ ions.[18] POM anions in polymer films can provide a secondary mechanism

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to store charge due to the fact that they can present reversible redox reactions interchanging electrons without any change in the original structure, which makes these hybrid materials very interesting for battery electrodes[11,19] and for electrochemical sensors.[17]

Any of the possible electrochemical applications require constant composition and properties of the material along the device life. One unsolved question is if the POM is lost from the material during work (changing composition and properties) and how this interchange depends on the electrolyte constituent ions. In this paper we report the electrogeneration of Ppy films doped with the chromium-substituted Keggin polyanion $[SiCr(H_2O)W_{11}O_{39}]^{5-}$ and its electrochemical behavior in three electrolytes: the original Keggin salt, substituting the POM by perchlorate, and in lithium perchlorate.

## 2. Experimental Section

The polyoxometalate salt $(NBu_4)_4H[SiCr(H_2O)W_{11}O_{39}]$ was synthesized according to the described method.[20] Pyrrole (Jansen) was distilled at 59 °C under vacuum (50 Torr) and stored at low temperature in the dark before use. All other chemicals were reagent grade and were used as received. A platinum sheet with a surface area of 1 cm$^2$ was used as a working electrode, stainless steel having 3 cm$^2$ surface area was used as the counter electrode. A Ag/AgCl 1 M electrode was used as the reference electrode. Potentials in this work are referred to this electrode. All the experiments were done under ohmic drop compensation at room temperature and under nitrogen atmosphere. The hybrid films were prepared by electrochemical oxidation from fresh acetonitrile + 2% H$_2$O (v/v) solutions containing pyrrole and the POM anion in three-electrode cells (Metrohm). After generation, the coated electrode was rinsed with acetone, dried in hot air, and weighed. The film weight was evaluated by difference between the uncoated working electrode and the coated electrode, using a 4504 MP8 Sartorius ultramicrobalance ($10^{-7}$ g precision). Then the coated electrode was transferred into another cell with different electrolytes for control cyclic voltammetry at the potential range between 250 and −800 mV or 250 and −1000 mV. The presence of POM anions in the solutions was checked by UV−vis spectra (PU8700, Philips). A M273 PAR potentiostat−galvanostat, connected to a PS-5 IBM computer with M273 software from EG&G, was used for the electrogeneration and the electrochemical studies of the polymer films. Magnetic measurements were done with a SQUID magnetometer (Quantum Design MPMS-XL-5) at a magnetic field of 1 T in the temperature range 2−300 K. The sample was corrected from the sample holder previously measured under the same conditions. Direct current conductivity measurements were performed in the SQUID cryostat by the four contacts method using 25 mm diameter platinum wires attached to the films with graphite paste. To perform the magnetic and conductivity measurements the deposited films need to be removed from the working electrode; the films prepared for these measurements were deposited onto ITO electrodes (under the same synthesis conditions but with larger polimerization times) and then removed from the electrodes. Elemental analyses of the films were done with a Phillips XL-30 environmental scanning electron microscope (ESEM).

## 3. Results and Discussion

**3.1. Electrogeneration of the Hybrid Materials.** As can be seen in Figure 2, no obvious oxidation−reduction processes occurred on a clean platinum electrode in acetonitrile solutions
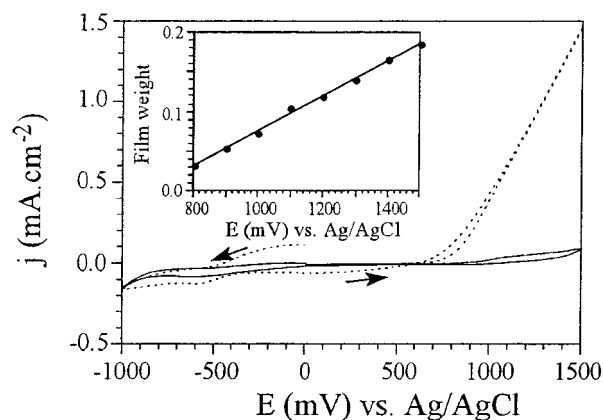


**Figure 2.** CV of a POM acetonitrile solution (1 mM) (solid line) and of the same solution after the addition of 0.1 M pyrrole (dashed line). $T = 25$ °C, $v = 20$ mV s$^{-1}$. Inset: Film weight as a function of the applied constant potential during 60 s in a fresh solution every time (working electrode, 1 cm$^2$ platinum electrode).
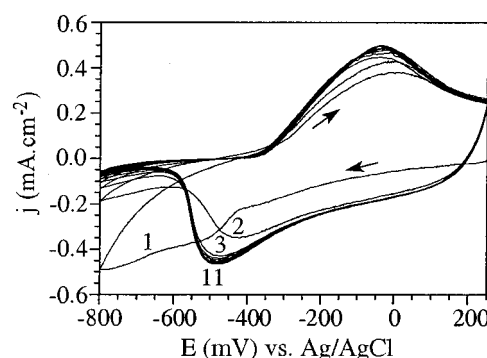


**Figure 3.** Consecutive voltammograms from a hybrid film in 5 mM $(NBu_4)_4H[SiCr(H_2O)W_{11}O_{39}]$ acetonitrile solution, $T = 25$ °C, $v = 20$ mV s$^{-1}$. The film was obtained by passing 100 mC through an acetonitrile solution with 0.1 M pyrrole and 1 mM POM under a constant potential of 1200 mV. Starting potential, 250 mV.

containing the POM in the studied potential range (between −1000 and 1500 mV). When pyrrole was present, the voltammograms show pyrrole oxidation−polymerization initiating at 750 mV.

To optimize the starting conditions for the electrogeneration of the films, we prepared several hybrid films by electrochemical oxidation of pyrrole at different constant potentials during 60 s from fresh acetonitrile + 2% H$_2$O (v/v) solutions containing 1 mM POM anion and 0.1 M pyrrole. No film was formed on the electrode by polarization at 700 mV or lower potentials. A thin yellow film and a thick dark blue film were formed on the electrode at 800 and 1500 mV, respectively. Whatever the potential of synthesis, the obtained films were extremely adherent and quite smooth and shiny. The weight of the rinsed and dried films increases linearly with the potential of synthesis (see inset in Figure 2). To check the electrochemical properties of the hybrid materials, we decided to generate reproducible films by passing 100 mC at 1200 mV in acetonitrile + 2% H$_2$O (v/v) solutions containing 1 mM POM anion and 0.1 M pyrrole. After electrosynthesis each coated electrode was controlled by cyclic voltammetry from 250 to −800 mV at a scan rate of 20 mV s$^{-1}$ in different electrolytes without pyrrole.

**3.2. Cyclic Voltammograms in $(NBu_4)_4H[SiCr(H_2O)-W_{11}O_{39}]$ Acetonitrile Solution.** Figure 3 shows consecutive cyclic voltammograms (CV) obtained from a coated electrode in 5 mM $(NBu_4)_4H[SiCr(H_2O)W_{11}O_{39}]$ acetonitrile solution. After the two initial cycles, stable voltammograms were
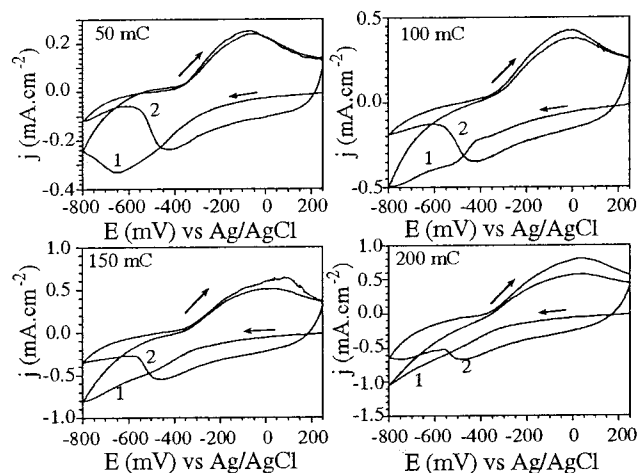
**Figure 4.** First and second cycles, in 5 mM (NBu$_4$)$_4$H[SiCr(H$_2$O)-W$_{11}$O$_{39}$] acetonitrile solution, obtained in four films with different thickness. $T = 25$ °C, $v = 20$ mV s$^{-1}$. Films were electrogenerated by passing different charges (50, 100, 150, and 200 mC) in acetonitrile solutions with 0.1 M pyrrole and 1 mM POM at 1200 mV.



**Figure 5.** Charge consumed in the first cathodic scan (QC1, black circles) and weight lost during the two first cycles (white circles) as a function of the film weight for the Ppy/POM films prepared by passing different charges (50, 100, 150, and 200 mC) in acetonitrile solutions with 0.1 M pyrrole and 1 mM POM at 1200 mV. Inset: Difference between the charge consumed in the first and second cycles (Q1 − Q2) as a function of the film weight for the same films.

observed on the consecutive cycles. A large anodic (at about −50 mV) peak and one cathodic (at about −500 mV) peak, related to the polymer redox processes, are observed.[21,22] The great degree of overlap of the consecutive voltammograms, after the two first cycles, and the absence of any cloud, indicative of the formation of reduced blue POM species around the electrode during the initial cathodic sweep, indicate the great stability of the redox properties of the film, without POM exchange toward the solution. These results point to a cation (NBu$_4$$^+$) interchange (insertion/release) during cycling in order to keep the electroneutrality inside the film.

During the first reduction scan the cathodic peak appears at more negative potentials, the involved charge being higher than that of the subsequent cycles. This feature, referred to as first scan effect in the literature, has been observed in different systems and attributed to dopant anion expulsion,[23] structural changes,[23−27] cation doping,[28] water effect, or changes in the morphology.[27] To study the influence of the film thickness on this first scan effect, different films were electrogenerated by passing 50, 100, 150, and 200 mC under a constant polarization potential of 1200 mV and then were submitted to voltammetric control. Weights of the clean platinum electrode, the coated (dry) electrodes after electrogeneration, and the coated and dry electrodes after the two initial cycles of control were determined. As the weight of the electrogenerated film increases (and therefore its thickness), the cathodic peak on the initial voltammograms, which appears around −650 mV when the film was prepared with 50 mC (Figure 4), gradually shifts toward more negative values, being out of the studied potential range for the thicker films (Figure 4).

A detailed study of the consumed charges in the cathodic (QC) and anodic (QA) scans of the different cycles in the CV and the weight loss after the two first cycles show (i) a linear relationship between the charge involved in the first cathodic scan (QC1) and the film weight, or thickness (Figure 5); (ii) a linear relationship between the weight loss during the two initial cycles of control and the film weight (see Figure 5); and (iii) the difference between the consumed charge in the first and in second cycles (Q1 − Q2) as a function of the film weight increases with increasing the film weight for the thinner films (50 and 100 mC) and decreases with increasing film
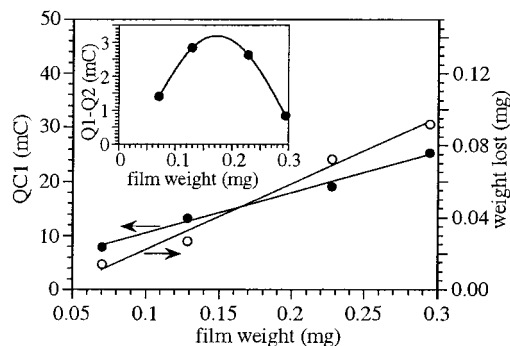
weight/thickness for the thicker films (150 and 200 mC); i.e., they present a maximum at intermediate thickness (see inset in Figure 5).

All these experimental facts point to a first scan effect due to structural changes produced in a compacted and just electrogenerated film in order to allow the penetration of cations during the initial cathodic sweep. Symmetric effects were observed and reproduced under control of cathodic polarizations for prevalent anion insertion processes.[29,30] This structural effect is more important for thicker films due to cross-linking effects present in films for long polymerization times (high charges at constant potential).[31] The diameter of the open pores diminishes and the electrochemically stimulated penetration of cations is more difficult, requiring more energy and promoting the cathodic shift of the maxima. This cross-linking also has a participation on the anodic potential shift of the anodic maxima at increasing thickness of the polymer film (Figure 4).

To better understand these structural effects it is important to note that during the exchange process a change of volume occurs in films of conducting polymers along redox processes. This property has given rise to the development of artificial muscles: the electrochemically induced expulsion of ions to the solution promotes the compaction of the structure with destruction of free volume, which is occupied by the conformational movements of the polymeric chains during the electrochemical process. The opposite processes occur during penetration of ions from the solution.[20,30] In our case the electrogenerated films are compacted structures, requiring extra energy (cathodic overpotential) to open the structure, allowing the penetration of cations during reduction

As mentioned before, after the two initial cycles, the films present stable CV, suggesting that the POM anions are trapped in the polymer network and cannot be released. In this case, the charge compensating ions must be the cations present in solution (NBu$_4$$^+$), whose movement is characterized by diffusion and migration.[32−34] This insertion and release of cations should cause an increase/decrease of the film weight in the reduced/oxidized state (when cations are inserted/ejected, respectively). To check this hypothesis we have weighed the dried films in both their reduced and oxidized states. These measurements show a weight increase of the film in the reduced state, related to that of the oxidized film, of about 10−15%, confirming the movement of NBu$_4$$^+$ during the redox processes. To check if the insertion/release of the big NBu$_4$$^+$ cation is controlled by diffusion, we have performed the CV of the film at different scan rates ($v$) in a 5 mM (NBu$_4$)$_4$H[SiCr(H$_2$O)W$_{11}$O$_{39}$] aceto-
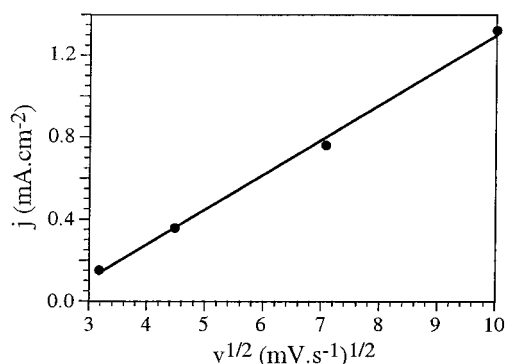
**Figure 6.** Anodic peak current density as the function of $v^{1/2}$, $T = 25$ °C, scan rate from 10 to 100 mV s$^{-1}$. Film formed by passing 50 mC in acetonitrile solutions with 0.1 M pyrrole and 1 mM POM at 1200 mV.
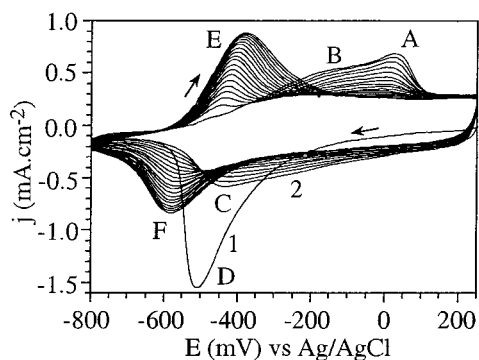


**Figure 7.** CV in 0.1 M LiClO$_4$ acetonitrile solution of a just electrogenerated hybrid film, $T = 25$ °C, $v = 20$ mV s$^{-1}$. Film formed by passing 150 mC in acetonitrile solutions with 0.1 M pyrrole and 1 mM POM at 1200 mV.

nitrile solution. The anodic peak current density follows a linear dependence with $v^{1/2}$ (Figure 6), indicating that the diffusion of cations in the polymer film is rate-controlling. Anodic and cathodic peaks shift toward more positive and negative potentials, respectively, when the scan rate increases, while the redox potential $E_o$ appears to be quite independent of the scanning rate.

**3.3. Cyclic Voltammograms in 0.1 M LiClO$_4$ Acetonitrile Solution.** Figure 7 shows the CV evolution during 20 consecutive cycles in 0.1 M LiClO$_4$ acetonitrile solution of a Ppy/POM film prepared by passing 150 mC through acetonitrile solutions containing 0.1 M pyrrole and 1 mM POM, at a constant potential of 1200 mV. A very sharp and intense peak (D) is only observed on the initial cathodic voltammogram at −500 mV. A blue cloud is formed around the electrode along with this electrochemical reduction. On the first anodic voltammogram we observe a peak at 50 mV (peak A) and a shoulder at −150 mV (noted B). The consecutive cycles show decreasing intensities on both peak A and shoulder B, while a new peak (E) appears and rises at more negative potentials (−440 mV) shifting toward less negative potentials (after 20 cycles peak E is at −380 mV). After about 10 cycles, peak A and shoulder B have disappeared. The second cathodic scan shows only a peak at ca. −400 mV (noted C), whose intensity decreases on the subsequent cycles (no blue cloud is observed around the electrode) while a new cathodic peak (F) appears at more negative potentials (−550 mV). After about eight cycles peak C has disappeared.

The sharp initial change (peak D) is related to an electrodissolution process involving the POM anions and pyrrole oligomers.[21] The subsequent continuous changes can be attributed to a progressive interchange of the POM anion of the film with
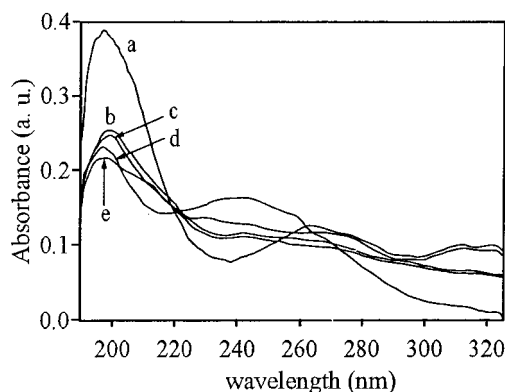


**Figure 8.** Absorbance spectra obtained for different solutions: (a) reference solution 6 × 10$^{-6}$ M POM in 0.1 M LiClO$_4$ acetonitrile; (b−d) the solutions after five control cycles from 250 to −700, −500, and −300 mV, respectively; and (e) the solution after a reduction cycle from 250 to −800 mV. A just electrogenerated film was checked every time in a 0.1 M LiClO$_4$ acetonitrile solution at $v = 20$ mV s$^{-1}$.

**TABLE 1: Weight Loss of the Film after Cycling, POM Content in Solution after Cycling, and C/W and C/Cl Atomic Ratio in the Film at Different Reduction States (see the text)**

| film state | weight loss (mg) | POM in solution (mg) | C/W | C/Cl |
|---|---|---|---|---|
| 5 cycles, 250 mV/−300 mV | 0.0152 | 0.021 | 10.5 | 150 |
| 5 cycles, 250 mV/−500 mV | 0.0160 | 0.027 | 12.9 | 160 |
| 5 cycles, 250 mV/−700 mV | 0.0131 | 0.028 | 13.2 | 570 |
| 0 cycles, 250 mV/−800 mV | 0.0105 | 0.013 | 8.2 | |

perchlorate ions from the solution. To check this hypothesis, the POM content was followed in the background solution by UV−vis spectroscopy, and the film composition, at different reduction stages, was studied by EDX. Figure 8 shows the UV−vis spectra obtained from (a) a reference solution containing 6 × 10$^{-6}$ M POM in 0.1 M LiClO$_4$ acetonitrile; (b−d) the solutions resulting from five oxidation/reduction cycles of just electrogenerated films followed by reduction scan from 250 mV to −700, −500, and −300 mV, respectively at $v = 20$ mV s$^{-1}$ in a 0.1 M LiClO$_4$ acetonitrile solution; and (e) the solution resulting from a unique reduction scan from 250 to −800 mV of a just electrogenerated film in a 0.1 M LiClO$_4$ acetonitrile solution at $v = 20$ mV.s$^{-1}$.

From the curve a in Figure 8 we deduce that the main POM absorbance occurs at about 200 nm. Consequently, we established a calibration line (absorbance−concentration) by using different POM concentrations. With this calibration line we have estimated the POM content in the different solutions by measuring their absorbances at 200 nm. These values are listed in Table 1.

About 50% (0.013 mg) of the total released POM (0.028 mg) leaves the film during the first reduction scan (peak D, Figure 7). The remaining POM is released during the following cycles. It is important to note that the amount of POM present in the solution is a maximun when the cathodic scan finished at −500 mV, and remains constant when the reduction scan goes ahead and finishes at −700 mV. These results suggest that partial expulsion of POM anions takes place during reduction processes between −300 and −500 mV; this corresponds to peak C. So, we can conclude that peaks C and D correspond to the polymer reduction along with a partial expulsion of the POM. These conclusions are also supported by EDX results (see Table 1) that show an increase in the C/W ratio (i.e., a decrease of the POM content in the film) when the reduction scan goes from −300 to −500 mV, whereas the C/W ratio remains constant
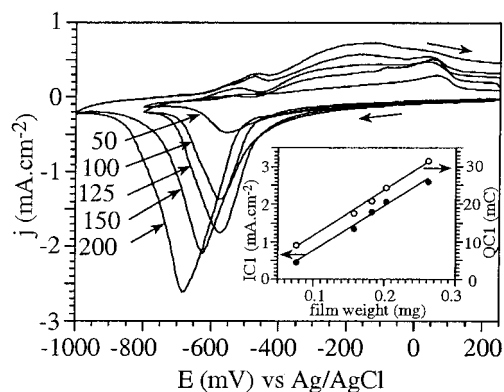
**Figure 9.** CV of the Ppy/POM films in 0.1 M LiClO$_4$ acetonitrile solutions, $T = 25\ °C$, $v = 20$ mV s$^{-1}$. The films were prepared by passing 50, 100, 125, 150, and 200 mC in acetonitrile solutions with 0.1 M pyrrole and 1 mM POM at 1200 mV. Inset: First cathodic peak current (IC1) and charge (QC1) as a function of the film weight.

when the reduction scan goes from $-500$ to $-700$ mV, confirming that no POM release occurs between $-500$ and $-700$ mV. Furthermore, the release of POM must be accompanied by cation (Li$^+$) insertion in order to keep the electroneutrality of the POM retained inside the film, because the weight loss of the film is smaller than that related to the POM mass released to the solution.

Another important point showed in Table 1 is the fact that the C/Cl ratio follows the opposite behavior as the C/W ratio. This result indicates that the ClO$_4^-$ release from the film takes place during the electrochemical reduction from $-500$ to $-700$ mV but not during reduction from $-300$ to $-500$ mV. Therefore, peak F (at $-600$ mV) corresponds to polymer reduction along with ClO$_4^-$ release.

The cathodic peaks can also be easily assigned from their variation from cycle to cycle. Thus, peak A, which is very similar to that observed in (NBu$_4$)$_4$H[SiCr(H$_2$O)W$_{11}$O$_{39}$] solution (Figure 3), should correspond to polymer oxidation along with cation (Li$^+$) release. This Li$^+$ is inserted during the reductions (peaks C and D). In fact, peak A disappears when no more Li$^+$ is inserted (after about eight cycles). Peak E must be associated with polymer oxidation along with anion (ClO$_4^-$) insertion. A confirmation of this assumption comes from the fact that peak F (associated to a release of ClO$_4^-$) can only be observed after the appearance of peak E.

To check the effect of the film thickness on the first cycle of the CV, we have prepared several films by passing different polymerization charges (50, 100, 125, 150, and 200 mC) under the same experimental conditions as above. These films are controlled in LiClO$_4$ acetonitrile solutions between 250 and $-1000$ mV for the thickest films (those electrogenerated with 150 or 200 mC) or between 250 and $-800$ mV for the thinnest ones (electrogenerated with 50, 100, or 125 mC). The first cathodic voltammogram of all the films shows a sharp cathodic peak. At the same time a blue cloud is observed around the electrode. The position of this peak shifts toward more negative potentials as the film weight increases (Figure 9). Such observation supports the idea of an electrochemically induced conformational relaxation of the compacted polymeric structure, which is more difficult to achieve in the thicker films, as the penetration of cations from the solution through the pores is more difficult.[29,30] Both, the peak current (IC1) and the cathodic charge (QC1) linearly increase with the film weight (inset Figure 9).

We have also measured the weight loss of these films after the first two cycles. This weight loss linearly varies with the
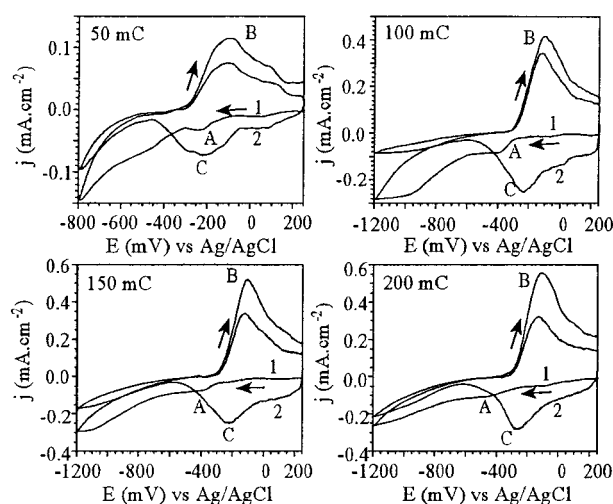


**Figure 10.** CV of the Ppy/POM films in 0.1 M (NBu$_4$)ClO$_4$ acetonitrile solutions, $T = 25\ °C$, $v = 20$ mV s$^{-1}$. The films were prepared by passing 50, 100, 150, and 200 mC in acetonitrile solutions with 0.1 M pyrrole and 1 mM POM at 1200 mV.

film thickness from 60% for the thinnest film to 3% for the thickest one. This result suggests the simultaneous presence of an electrodissolution process.[35] The percentage of electrodissolved material decreases as the film thickness increases, supporting again the presence of more cross-linked molecular structures in the films electrogenerated by longer polarization times.[31]

**3.4. Cyclic Voltammograms in 0.1 M (NBu$_4$)ClO$_4$ Acetonitrile Solution.** The above results show that when the hybrid materials are controlled in solutions containing only big POM anions and NBu$_4^+$ cation, the redox processes are under control of the cation interchange between the polymer and the solution. When the hybrid materials are controlled in LiClO$_4$ solution containing small anions, the redox process involves a partial interchange between POM anions present in the film and ClO$_4^-$ from the solution. Under these conditions both, Li$^+$ insertion/release and ClO$_4^-$ release/insertion are present during cathodic/anodic sweeps, respectively. After about 10 cycles only the ClO$_4^-$ interchange is present. All that points to a prevalent cation insertion/release (cathodic/anodic sweep) affected by the cation size during the first cyclic voltammogram, which also influences the presence or not (Li$^+$ or NBu$_4^+$solutions, respectively) of a partial electrodissolution process.

To check these effects, hybrid films prepared by passing 50, 100, 150, and 200 mC under the same conditions as above were now controlled by cyclic voltammetry in 0.1 M (NBu$_4$)ClO$_4$ acetonitrile solution. Figure 10 shows the first two cyclic voltammograms. An important first scan effect is observed, the concomitant maximum (peak A) shifts from a small cathodic shoulder at about $-250$ mV in the thinnest film to more negative potential as the film weight increases, reaching values of about $-400$ mV in the thickest film. The second and successive cycles only show one cathodic peak (C) at $-250$ mV and one anodic peak (B) at $-100$ mV (Figure 10). The current density always increases from the first to the second cycle and then remains constant during the next 20 cycles.

The differences (QC2 $-$ QC1) and (QA2 $-$ QA1) between the charges involved in the first and the second cathodic and anodic scans become larger as the film weight increases. The film weight of the reduced film (when the stationary state is attained) is higher than that of the oxidized film, suggesting cation (NBu$_4^+$) insertion for charge compensation (rather than anion release) during film reduction (peak C). Accordingly, peak
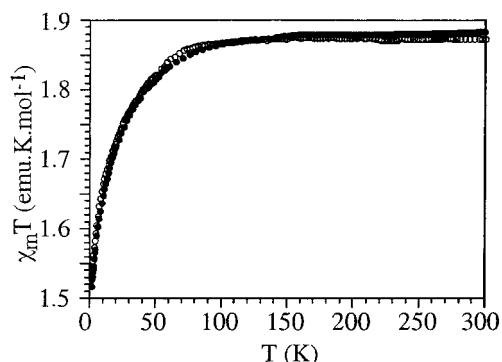
**Figure 11.** Thermal variation of the product of the susceptibility times the temperature for the Ppy/[SiCr(H$_2$O)W$_{11}$O$_{39}$]$^{5-}$ hybrid film (filled circles, normalized at room temperature) and of the NBu$_4^+$ salt of the same anion (empty circles).

B is attributed to the polymeric oxidation along with NBu$_4^+$ release for charge compensation, in a similar process as those described for the anodic peak B observed in Figure 3 and the anodic peaks A and B in Figure 9.

After two cycles 10% of the film weight is lost, and the presence of POM in the solution is detected by UV−vis spectroscopy. The POM concentration remains constant during the following cycles. These results indicate that the POM anions are retained in the polymer matrix after the two initial cycles. The weight loss can be due to the presence of an electrochemically induced dissolution of polypyrrole oligomers with POM anions such as that observed in LiClO$_4$ solution. The small weight lost and the high anodic potential ($-250$ mV vs $-500$ mV in the LiClO$_4$ solution), does not allow the observation of any cloud around the electrode as above. At this potential the POM anion is in its oxidized and colorless state.

After cycling, the film electrogenerated by passing 100 mC is controlled by cyclic voltammetry in fresh 0.1 M (NBu$_4$)-ClO$_4$ acetonitrile solution at different scan rates ($v$). As the scan rate increases, the anodic and cathodic peaks shift toward more positive and negative potentials, respectively. However, the redox potential $E_o$ appears to be quite independent of the scanning rate. The anodic peak current density follows a linear variation with $v^{1/2}$, indicating that the oxidation process of the hybrid material in this solution is controlled by the diffusion of the inserted ion.

**3.5. Physical Characterization of the Films.** The dc electrical conductivity of a film prepared onto an ITO electrode shows an activated conductivity with a high room-temperature conductivity (0.33 S cm$^{-1}$) and a thermal behavior that follows a law of the type $\sigma = aT^\alpha$ with $a = 10^{-6}$ and $\alpha = 2.2$. This result agrees with the idea that the polypyrrole is in its oxidized state and that the POM act as a counterion in the synthesis procedure. To confirm the presence of the [SiCr(H$_2$O)W$_{11}$O$_{39}$]$^{5-}$ POM we have performed magnetic susceptibility and isothermal magnetization measurements on the same film used for the dc conductivity measurements. These clearly show that the POM is inserted into the polymer matrix during the electropolymerization process. Thus, the product of the magnetic susceptibility times the temperature for the film shows the same paramagnetic behavior as that of the NBu$_4^+$ salt of the same POM anion (Figure 11). Moreover, from the normalization factor required to scale these two measurements we can conclude that the pyrrole/POM ratio is approximately 22. This result implies that the number of pyrrole monomers ($n$) per cationic charge is approximately 4.4, in good agreement with the results obtained for other hybrid films formed by polypyrrole and different

POM[19,22] and with the results of the elemental analysis of the films that show a pyrrole/POM ratio of approximately 20, i.e., $n = 4$.

## 4. Conclusions

Hybrid films of polypyrrole doped with the POM anion [SiCr(H$_2$O)W$_{11}$O$_{39}$]$^{5-}$ are electrogenerated from acetonitrile solutions containing pyrrole and the POM anion, by polarization under constant potential. The first cathodic scan of the CV always shows a nonsteady state behavior with a cathodic shift of the maxima attributed to the extra energy required to open, under electrochemically stimulated conformational relaxation of the polymeric chains, the compact structure of the just electrogenerated films, allowing the injection of cations from the solution. The control of the films in solutions containing the pristine polyoxometalate salt (POM and NBu$_4^+$) shows steady state voltammograms. Only one cathodic and one anodic peak are present, corresponding to the insertion/release of the NBu$_4^+$. After the two initial cycles, the POM anions remain stable in the polymer matrix, as deduced from ultramicrogravimetric and spectroscopic determinations. When the control solution contains LiClO$_4$ as electrolyte, the POM is exchanged with the ClO$_4^-$ anion during the cycling process, and the voltammograms show a continuous evolution from the original redox couple to a new one. In this case, during the first cathodic scan an important weight loss is observed, due to an electrochemically induced dissolution of POM and pyrrole oligomers. The substitution of lithium by NBu$_4^+$ in the last salt promotes an initial loss of material followed by a stabilization of the voltammograms, related to NBu$_4^+$ exchange between the film and the solution. Ionic interchanges, once the steady state is attained, are under diffusion control. Those results show the important effect of the cation present in solution on both the material composition and their stability during cycling. The magnetic properties of the film are identical to those of the NBu$_4^+$ salt of the POM, confirming the incorporation of the POM during the electrogeneration of the film. Furthermore, these magnetic measurements have allowed an estimation of the number of pyrrole monomers per anionic charge, which was close to 4, the value found by elemental analysis. Finally, the high room-temperature electrical conductivity confirms the presence of the polymer in its oxidized state.

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