Articles

Electrochemical and Chemical Syntheses of the Hybrid Organic−Inorganic Electroactive Material Formed by Phosphomolybdate and Polyaniline. Application as Cation-Insertion Electrodes

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We report a hybrid organic−inorganic electroactive material composed of a conducting polyaniline matrix and the phosphomolybdate anion ($[PMo_{12}O_{40}]^{3-}$) as the active inorganic component. The material can be prepared electrochemically as thin films or chemically in the bulk, in the absence of other competing anions. The phosphomolybdate anion is anchored within the polymer matrix and not exchanged upon reduction. The material presents good conductivity and electroactivity, and it represents an example of electrodes that can take advantage of the electroactivity of zero-dimensional molecular species. A preliminary analysis of the material as a cathode in reversible lithium batteries is discussed.

Introduction

Active materials used as cathodes in the development of secondary (reversible) lithium batteries have varied along the years since the initial use of TiS_2. Nevertheless, all of them share several common characteristics such as reversible redox behavior and open structures that allow for ionic insertion/deinsertion processes concomitant to the reduction/oxidation reactions.

The fact that these cathode materials require electronic as well as ionic conduction during their working process explains why all of them are in fact extended solids usually presenting layered or channel structures and why cluster or molecular compounds have never been considered for this task.

The solids used for these so-called insertion electrodes are most frequently chalcogenides or oxides of transition metals,[1] strongly oxidant compounds that incorporate cations (normally Li or protons) into their lattices upon reduction and eliminate them upon oxidation in a reversible way. They react in front of lithium metal or lithium insertion anodes which provide the Li^+ ions in a process with a source-sink mechanism. Among the compounds most frequently studied we can mention TiS_2, WO_3, MoO_3, V_2O_5,[2] and more recently $LiMn_2O_4$, $LiCoO_2$, and $LiNiO_2$,[3] the latter formulated in their discharged state.

A different category of materials is formed by the large family of conducting organic polymers such as polyaniline, polypyrrole, or polythiophene. Their use as active materials for electrodes is more recent and began when the reversibility of the redox properties of these conjugated polymers was realized and exploited in addition to their good electronic conductivity. The light weight and processability of these polymers represented at the time a great promise for improving the technical characteristics of rechargeable lithium cells and “plastic” batteries were envisaged.[4]

The working mechanism of these organic electrodes is nevertheless quite different from that of the inorganic solids. The conjugated chains are formed by oxidative polymerization with the incorporation of doping anions and the reduction of this material takes place with deintercalation of anions rather than with incorporation of cations.[4,5] This fact affects negatively the energy densities of cells making use of this kind of polymeric electrodes since the electrolyte needs to function for storage of anions and not only for ion transport as in the source-sink Li-ion batteries.[6] This, together with severe problems of high self-discharge rates has made organic electrodes to lose ground in favor of inorganic active materials in the race for achieving improved performance for the commercial competitiveness of rechargeable lithium batteries. Recently there have

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been new efforts to modify conducting polymer electrodes in order to convert them into cation-inserting systems. This has been accomplished by doping the polymer with organic anionic polyelectrolytes,[7−10] propanesulfonic acid,[11] *o*-aminobenzenesulfonic acid,[12,13] camphorsulfonic acid,[14] or by self-doping.[11−13] Nevertheless in all those cases the immobilized anions are not electrochemically active.

We have explored the possibility of making cation-inserting electrodes for secondary batteries by doping bulky electroactive inorganic anions into the conducting polymer matrix.[15−17] A similar approach but based on organic electroactive polysulfide anions has been recently reported.[10,18−22]

Polyoxometalates (POMs) are ideal models for this kind of "*molecular battery*". They resemble clusters of metal oxides both from the structural and electronic point of view; they are formed by a small number of metal centers (typically 6−18 W or Mo) coordinated by bridging oxygen atoms, present well-known structures and undergo reversible multielectron reduction processes.[23] Nevertheless, the zero-dimensionality derived from their molecular nature has caused them to be ignored as active compounds for electrodes or for any kind of material where collective properties were needed.[24] Polyoxometalates have been extensively studied from a chemical point of view and have been used in catalysis and photocatalysis, either as homogeneous catalysts or supported onto polymers. Some examples are known of polyoxometalates doping conducting organic polymers such as polyaniline for application in catalysis, but in all the cases we have found, other anions coexist as the doping species with the POMs, which are therefore effectively diluted.[25−34]

The phosphomolybdate anion (PMo12), used in the present work, belongs to a large family of heteropolyanions with the so-called Keggin structure, where a tetrahedral XO_4 core ($X = P$ in this case) serves as a template for the aggregation of 12 MoO_6 or WO_6 octahedra sharing corners and edges. In its acid form $H_3PMo_{12}O_{40}$ is both a strongly oxidizing species and a strong acid.

We have recently reported the formation of the hybrid electrode formed by polypyrrole and PMo12 but found that the polypyrrole matrix was too prone to decomposition.[16] In this paper we describe the hybrid formed by the same PMo12 anion dispersed into the more stable polyaniline (PAni) matrix. Our aims with this system can be summarized in the following three goals:

(i) To demonstrate the possibility of synthesizing hybrid materials based on a polyaniline (PAni) matrix with the phosphomolybdate anion (PMo12) as the *only* doping species. To our knowledge this is the first such report.

(ii) Establish the behavior of the hybrid upon cycling in terms of anion/cation insertion.

(iii) Explore some of the possible applications of a bulk solid material that incorporate molecular species such as PMo12. This provides an opportunity to harness the molecular properties of PMo12 and its derivatives (electrochemical, photochemical, magnetic) within the framework of a solid material. This is something usually out of reach for molecules with a few exceptional examples (TTF salts, fullerenes), and this approach shows a way to do it. In the present report, electrochemical properties of PMo12 are tackled for energy storage applications. It should be remarked that PMo12 and polyoxometalates in general have a large tradition in chemistry (structural, spectroscopy, catalysis) but not in materials science, where, we believe, they have a great potential (energy storage, electrochromism, photoconductivity, photoconversion).

Experimental Section

Reagents. Aniline from Aldrich was distilled under vacuum prior to use for both chemical and electrochemical syntheses; phosphomolybdic acid was purchased from Aldrich and used without further purification. Water content in $H_3PMo_{12}O_{40}\cdot 17H_2O$ was determined by thermogravimetric analyses. NMP (1-methyl-2-pyrrolidinone) solvent (Aldrich) was used without further purification. Battery electrolyte mixture was made by mixing EC (ethylene carbonate, no further purification) and anhydrous DME (dimethoxyethane) in a 1:1 ratio. $LiClO_4$ electrolyte salt was dried at 155 °C under dynamic vacuum for 12 h. Once made, battery electrolyte solution was purged with argon before use.

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Measurements. A Carlo Erba CHN EA 1108 system was used for elemental analyses. Mo was analyzed by inductively coupled plasma (ICP) using a Jobin Yvon JY38 apparatus. The electric resistivity of pelletized samples was measured by the Van der Pauw technique; samples of the chemically prepared hybrid materials were dried under dynamic vacuum until a constant weight was achieved and pressed into pellets onto which four copper leads were attached with silver paint. Infrared spectra were recorded as KBr pellets with a Nicolet 710 FTIR spectrophotometer. Electrochemical studies were carried out with a computer-controlled EG&G PAR207A potentiostat/galvanostat interfaced to a three-electrode cell with Ag/AgCl reference electrode and Pt counter electrode for characterization in aqueous media, and Li metal as reference and counter electrode for characterization in organic media. As electrolytes we used $HClO_4$ and $LiClO_4$ 1 M for aqueous and organic media, respectively. Compact reversible electrochemical cells were set up in Swagelock test cells[35] using a Labconco 50700 glovebox that allows for water and oxygen removal to less than 1 and 5 ppm, respectively. Additionally, homemade containers described in the Supporting Information (Figure S1) were used for the setup of three-electrode cells that included a Li metal reference electrode. Li foil (16−13 mm diameter and 0.1 mm thick) was used in both cases as negative electrode, an intimate mixture of the hybrid material and carbon Super P (20%) as the positive electrode and a solution of $LiClO_4$ 1 M in a 1:1 mixture of EC/DME was used as electrolyte. The cells were tested with charge/discharge cycles performed with an ARBIN model BT2042 potentiostat.

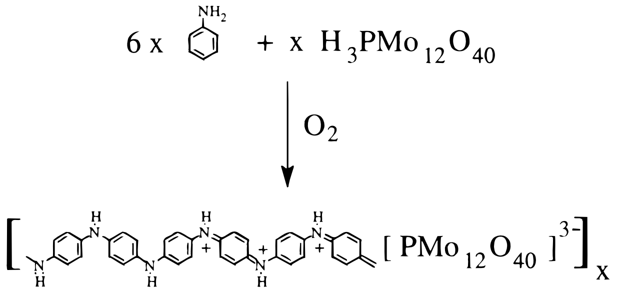
Chemical Synthesis of the Hybrid PAni/PMo12. The chemical synthesis of the hybrid material was carried out by direct addition of pure aniline to solid phosphomolybdic acid. Otherwise, mixing solutions of the reactants give only soluble oligomeric products. Thus, 1 mL of aniline was added directly to 5.00 g of $H_3PMo_{12}O_{40}$. The two reagents were mixed by stirring with a glass rod and reaction was evidenced by the formation of a black paste and a deep blue solution (indicating the oxidation of aniline and reduction of the anion). Stirring was continued until the mixture turned into a black-green powdery solid (**1**, ca. 3 min). Experimental analyses of **1**: 15.27% C, 3.199% N, 1.545% H. Then 5.00 g of the powder **1** were added to 40 mL of water, and the mixture was bubbled with O_2 for at least 24 h with magnetic stirring. Finally a black precipitate was obtained, filtered, and dried under dynamic vacuum.

Chemical analyses: PAni/PMo12, experimental: 24.25% C, 4.29% N, 1.64% H, 40.87% Mo. Calcd for $C_6H_5N(PMo_{12}O_{40})_{0.116}$ (FW = 302.49): 23.82% C, 4.63% N, 1.66% H, 44.15% Mo.

Electrochemical Synthesis of the Hybrid PAni/PMo12. The electrochemical synthesis of the hybrid material was carried out by multiple cyclic voltammograms using Pt foil as working electrode, Ag/AgCl as reference electrode, and Pt coil as counter-electrode. The black-green powder **1** described in the chemical synthesis section above was used as the starting reagent. Thus 5 g of the powder **1** were dissolved in 100 mL of water, and the solution placed into a three-electrode cell. The hybrid material was obtained as a thin film onto the working electrode by means of repeated cyclic voltammetry (12 cycles) between 0.9 and −0.2 V (vs Ag/AgCl) at a scan rate of 1 mV/s. Chemical analysis: PAni/PMo12, experimental: 26.390% C, 4.932% N, 1.690% H. No Mo analysis was performed due to the small amount of sample obtained electrochemically.

Battery Analyses. Use of the hybrid PAni/PMo12 as cathode in a lithium reversible cell presented initially some difficulties due to partial dissolution of the material in the electrolyte within the compact cell. Solubility of conducting polymers such as PAni can be controlled by means of cross-linking of the polymer matrix in organic solvents.[36] Thus, cross-linking of the hybrid material was carried out by heating a suspension of 0.5 g of the material in 30 mL of NMP solvent. The solution was placed in a thermostated oil bath at 70 °C until total evaporation of the solvent took place (aproximately 90 h). After treatment, the material was washed with a mixture of 1:1 EC:DME (electrolyte mixture solvents), some dissolution of the material was still observed. Once dried under vacuum, the insoluble material was mixed with 20% of carbon Super P and was tested in a compact electrochemical cell vs Li.

Scheme 1



Results and Discussion

Synthesis. Polyoxometalates supported in polymers and in modified electrodes have been reported previously as a means to fix them on solid supports for catalytic purposes.[25−33,37] In these cases though other inert anions can effectively dope the polymer together with the active anion with minor if any effects on the catalytic properties of the material.

On the other hand, we pretend the synthesis of a hybrid material with the electroactive polyoxometalate as the only doping anion and therefore need to avoid the presence of other competing anions in the reaction mixture. Phosphomolybdic acid is a strong acid and oxidizing agent and can effectively lead to direct polymerization of pyrrole to form a solid hybrid material.[16] Phosphomolybdic acid also reacts with aniline as evidenced by the immediate change in color of the mixture. The resulting dark-green paste and blue solution are a clear indication of aniline condensation and PMo12 reduction, but a precipitate is not formed right away. This behavior implies slow kinetics that probably leads to the initial formation of soluble oligomeric polyaniline species. After longer reaction periods with exposure to air or oxygen the polyaniline-based hybrid begins to precipitate and eventually leads to a solid material with only PMo12 as doping counterion.

The polymerization reaction is much faster in the presence of oxidizing agents such as persulfate (used extensively in the synthesis of polyaniline) and perchloric acid; but in that case sulfate and perchlorate ions are indeed incorporated into the polymer matrix, reducing the effective amount of PMo12 in the material and thus reducing the capacity of the electrode.[17]

A schematic chemical equation of the synthesis reaction is pesented in Scheme 1, where the ratio of six aromatic rings per PMo12 molecule is the ideal expected value determined by the charge balance. It should be noted that PMo12 acts indeed as a catalyst since its reduced form is reoxidized by oxygen.

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Electrochemical synthesis of thin films of the hybrid material could only be achieved by using slow potential scan rates (1 mV/s). Faster scan rates led to no thin-film formation. Twelve scan cycles were sufficient to obtain thin films with a smooth and homogeneous surface and good adherence to the substrate. Greater numbers of cycles for the synthesis led to increased film thickness but also to a poorer adhesion of the additional material to the surface of the working electrode. No redox waves from PAni or PMo12 can be observed during thin-film formation, but they are later detected during electrochemical characterization of the film once rinsed and using a fresh electrolyte solution of $HClO_4$ 1 M.

Physical and Spectroscopic Properties. The hybrid materials maintain the plastic nature of their polymeric matrix and present high conductivity with maximum values of 0.5−1.0 S cm^{-1} for chemical and electrochemically synthesized materials, respectively. These materials are only partially soluble in certain organic solvents (NMP, THF). The soluble fractions before cross-linking (in THF) where analyzed by gel permeation chromatography (GPC) and were shown to contain chains of molecular weights between 5000 and 1000, relatively low when compared with other typical PAni polymers (100 000−1000). Cross-linking of this material as described above was performed in order to avoid this partial dissolution.

The presence of the PMo12 anion as part of the bulk material is indicated both by the chemical analyses (see Experimental Section) and by infrared spectroscopy. Figure 1a,b shows the FTIR spectra of the materials synthesized chemically and electrochemically. There is no apparent difference between the two spectra. The bands in the range 800−1100 cm^{-1} correspond mainly to PMo12[38] with some overlap from weak PAni bands in this region. Their assignment is made in Table 1. Bands characteristic of the PAni polymer appear in the region 1100−1600 cm^{-1} and have been assigned earlier to polyaniline in its emeraldine form.[28,39,40] The band at 1130 cm^{-1} indicates[40] the protonation of the PAni network.

Infrared analysis of the hybrid material shows some changes in the bands of the PMo12 anion anchored in the polymer matrix as compared to those of the free acid $H_3PMo_{12}O_{40}$ or its sodium salt (Table 1).[34,38] As could be expected, the inner P−O bonds are not substantially affected by the hybrid formation as indicated by the almost invariant frequency of vibration. The external Mo=O bond stretching shifts to slightly lower frequencies in going from the acid to the hybrid. But the main changes are observed in Mo−O−Mo vibrations, which involve the more basic oxygen atoms, i.e., those involved in the protonation of the anion. The characteristic Mo−O(corner shared)−Mo band shifts to lower frequencies in the hybrid whereas the Mo−O(edge shared)−Mo band shifts to higher frequencies. It must be noted that the difference between the frequencies of these two modes remains constant in going from the acid to the sodium salt but decreases markedly in the hybrid. This points out to a strong change in the environment of the anion dispersed in the polymer matrix, where it would be surrounded by the much more polarizable organic (polymer) cations and a substantially reduced amount of hydration water.

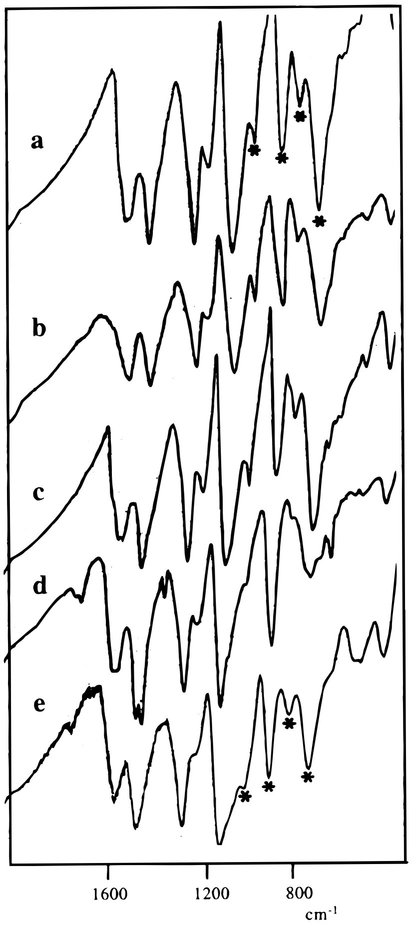

Figure 1. FTIR spectra for the hybrids PAni/PMo12 prepared chemically (a) and electrochemically (b). The other spectra correspond to one sample of PAni/PMo12 prepared electrochemically after discharge (electrochemical reduction) down to −0.2 V (a), −0.3 V (b), and −0.4 V (c) (all vs Ag/AgCl). Asterisks mark the peaks assigned to the $[PMo_{12}O_{40}]^{3-}$ anion (PMo12).

Electrochemical Studies. Figure 2 shows cyclic voltammograms obtained for PAni/PMo12 electrodes synthesized both chemically and electrochemically. For these experiments chemically synthesized PAni/PMo12 electrodes were made using a pressed pellet of the hybrid material ground and mixed with an equal amount by weight of graphite. Films of the electrochemically synthesized hybrids were analyzed immediately after preparation and once thoroughly washed with water. Both chemically and electrochemically synthesized materials present three well-defined redox waves characteristic of the PMo12 anion. For the electrochemically prepared material they appear at 0.31/0.38 V, 0.19/0.22 V, and −0.05/0.0 V (marked with * in Figure 2b), where the values indicate potentials at maximum intensity for the reduction/oxidation processes vs Ag/AgCl. Similar processes are observed for the chemically prepared hybrid (see Table 2). Two additional redox waves assigned to PAni (and marked with arrows in Figure 2) can be detected as shoulders

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Table 1. Frequency Values (cm^{-1}) and Assignment of FTIR Bands Observed for the Acid $H_3PMo_{12}O_{40}$, the Na Salt, and the Hybrid PMo12/PAni[a]

assignment	H_3 $PMo_{12}O_{40}$[38]	Na_3 $PMo_{12}O_{40}$	PAni/$PMo_{12}O_{40}$
ν_1 Mo−O(edge sh)−Mo	789 (760−800)	783	802
ν_2 Mo−O(corner sh)−Mo	871 (840−910)	865	830
$\nu_2-\nu_1$	82	82	28
ν_3 Mo=O(terminal)	968 (960−1000)	964	960
ν_4 P−O	1066 (1060−1080)	1064	1067

[a] Values in parentheses indicate the range of frequencies found in the literature.[34,38]

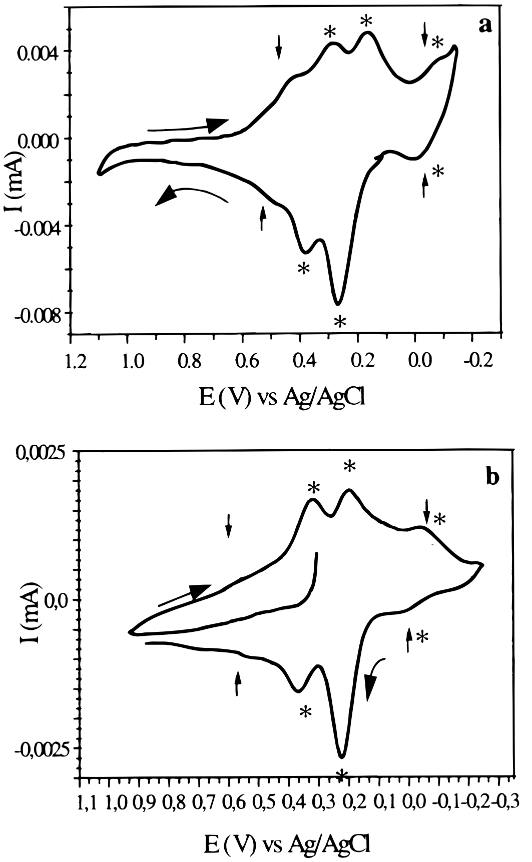

Figure 2. Cyclic voltammograms of PAni/PMo12 prepared chemically (a) and electrochemically (b). In both cases the electrolyte was 1 M $HClO_4$ and the reference electrode Ag/AgCl. Scan rates 0.05mV/s for (a) and 1 mV/s for (b).

Table 2. Hybrid PAni/PMo12 Redox Potentials (vs Ag/AgCl) in Aqueous ($HClO_4$) and Organic ($LiClO_4$) Media Sythesized Both Chemically and Electrochemically

aqueous				organic[a]		
chemical		electrochemical		chemical		
ox	red	ox	red	ox	red	assignment
0.5	0.4	0.7	0.5			PAni
0.39	0.29	0.38	0.31	0.23	−0.12	PMo12
0.26	0.18	0.22	0.19	−0.11	−0.3	PMo12
0.0	−0.05	0.0	−0.05	−0.55	−0.65	PAni-PMo12

[a] Values measured vs Li but indicated vs Ag/AgCl (−2.97 V difference).

(Table 2). The first one appears at around 0.4/0.5 V (for the chemically prepared hybrid) and around 0.5/0.7 V (for the electrochemically prepared analogue); the second one appears at −0.05/0.0 V vs Ag/AgCl, and it is partially overlapped with one of the PMo12 waves in both cases. The PMo12 redox values given above are in very good agreement with those obtained for the acid $H_3PMo_{12}O_{40}$ dissolved in 1 M $HClO_4$ solution and Pt working electrode.

To prove the absence of PMo12 anion deintercalation during cycling, we reduced the hybrid material potentiostatically at potential values where anion deintercalation takes place in normal conducting polymers. Infrared spectroscopy and cyclic voltammetry of the material were performed after each reduction to determine the permanence of the PMo12 in the hybrid. Figure 1c−e shows the FTIR spectra of the hybrid material after electrochemical reduction to −0.2, −0.3, and −0.4 V (vs Ag/AgCl). All three spectra show bands corresponding to the polymer matrix as well as those corresponding to the PMo12 anion, even at low reduction potentials (−0.4 V) bands of PMo12 are present. On the other hand, cyclic voltammograms of the hybrid electrode after each potentiostatic reduction in freshly prepared electrolyte solutions show the redox waves corresponding to the PAni/PMo12 hybrid material (as in Figure 2b) confirming the anchoring of the anion within the polymer.

After some hours exposed to air, we detected a change in color from colorless to yellow in some electrolytic solution used for reduction experiments. These yellow solutions are formed only when the hybrids are subject to potentials beyond the stability range of PAni. The same behavior has been reported earlier for the Polypyrrole/PMo12 hybrid material.[16] The nature of these colored solutions was analyzed by cyclic voltammetry; the solution obtained during the reduction of the hybrid electrode at −0.3 V showed a redox wave at values around 0.06/0.42 V (Figure 3a). We believe this wave corresponds to some organic decomposition material from the polymer due to overreduction or superficial corrosion of the polymeric matrix. In this solution no PMo12 redox waves were observed. On the other hand, the yellow solution that develops as explained before after treating the electrode at −0.4 V, does show waves corresponding to the PMo12 in solution (Figure 3b). No other redox wave for organic material was observed but could be overlapped by those of PMo12.

On the other hand, analyses of the hybrid material in organic medium ($LiClO_4$ in EC/DME) showed good activity (Figure 4). Redox waves corresponding to the PMo12 can be seen at potential values of 2.85/3.2, 2.68/2.86, and 2.32/2.42 V vs Li (−0.12/−0.23, −0.3/−0.11, and −0.65/−0.55 V vs Ag/AgCl), the latter possibly overlapped with PAni. The values of maximum intensity obtained for the material in organic electrolytes show displacements to more negative potentials with respect to those obtained in aqueous acidic media (Table 2). This seems to be a general trend and can be associated to the increase in negative charge of the anion in organic media, whereas in acidic media protonation of PMo12 upon reduction would keep the anion charge unchanged. Finally, the PAni redox wave typically observed at more oxidizing potentials is not

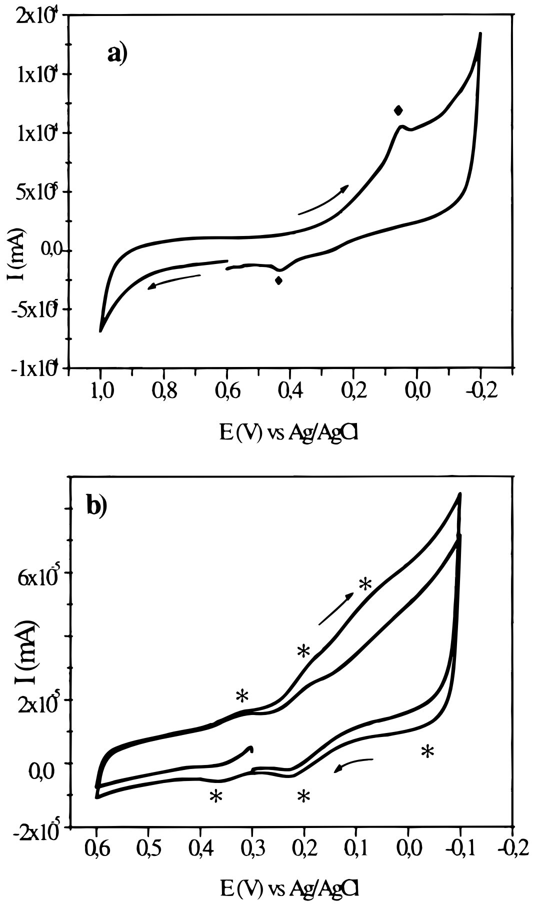

Figure 3. Cyclic voltammograms run on electrolyte solutions (1 M $HClO_4$) upon overreduction of the hybrid PAni/PMo12 (prepared electrochemically) and subsequent exposure to air (see text). (a) overreduction to −0.3 V vs Ag/AgCl. (b) overreduction to −0.4 V vs Ag/AgCl. Scan rate 20 mV/s in both cases. Asterisks in (b) mark the waves assigned to PMo12.

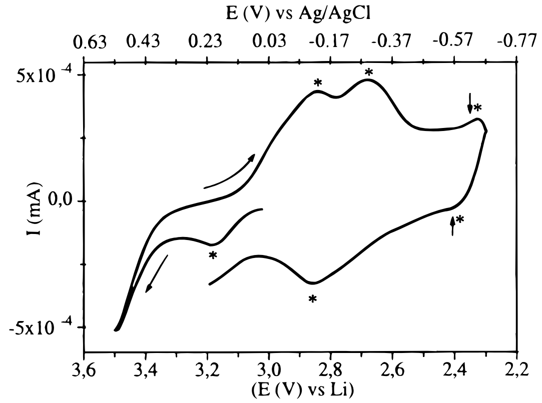

Figure 4. Cyclic voltammogram of the hybrid PAni/PMo12 prepared chemically and tested as a powder (with 20% carbon Super P) in a three-electrode compact cell (Figure S1) with Li foil as anode and reference electrode. Electrolyte 1 M $LiClO_4$ in EC/DME. Scan rate 0.5 mV/s. Asterisks mark redox waves characteristic of PMo12.

observed in organic media, possibly concealed by the oxidation of the electrolytic solution.

Battery Analysis. Initial analysis of the hybrid material as a cathode versus Li in compact reversible cells was made at low discharge rate: 50/C. The system give an open circuit voltage of 3.2 V. The potential range used for charge and discharge was 3.5 V and 2.3 V vs Li. The specific charge obtained was 53 A·h/kg (theoretical: 61.7 A·h/kg, 6e$^-$) corresponding to the charge needed to intercalate 5 Li ions/formula unit $[(C_6H_5N)_{8.6}PMo_{12}O_{40}]$. Figure 5 shows the charge/discharge curve obtained for the PAni/PMo12 hybrid material chemically synthesized. Two "plateaus" observed during discharge, around 3 and 2.8 V vs Li, correspond well to the redox waves for PMo12 in the cyclic voltammogram carried out in the same electrolyte solution (Figure 4), although the potential values change due to the different internal resistance of the cell. Due to the position and in relation with the CV in organic media, the first and second "plateau" are attributed to PMo12. There is evidence of extra activity around 2.5V attributed to the PAni−PMo12 activity.

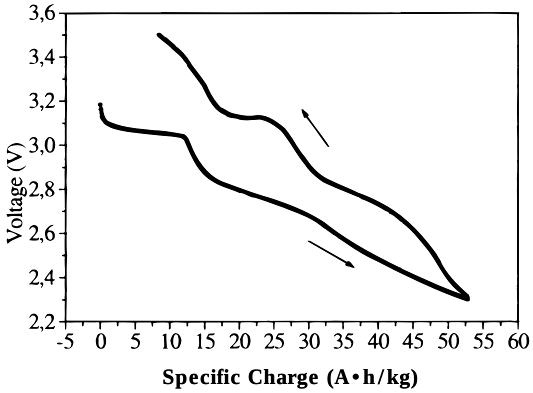

Figure 5. First discharge/charge curve for a lithium reversible cell using the hybrid PAni/PMo12 (plus 20 wt % carbon Super P) as cathode, Li foil as anode and a 1 M solution of $LiClO_4$ in EC/DME as electrolyte. Discharge and charge rates C/50.

As we mentioned in the Introduction, it is well-known that the anion deinsertion mechanism suffered by conducting organic polymers upon discharge in rechargeable lithium batteries gives specific energy problems.

In this work we have proved the anchoring of the electroactive PMo12 in the PAni matrix and its permanence in the solid upon reduction. To definitely prove the true cation insertion mechanism of the hybrid material we analyzed the lithium content of a PAni/PMo12 electrode after reduction in a reversible cell. Lithium analysis was performed after complete discharge of the cell down to 2.3 V. The charge that passed through the cell corresponded to 5.25 electrons/formula unit. Chemical analysis of the reduced hybrid material after discharge gave a lithium content of 5.35 ions/formula unit $[(C_6H_{4.8}N)_9PMo_{12}O_{40}]_x$, which is in very good agreement with the former value. This evidence in connection with the espectroscopic and analytical data confirming the permanence of PMo12 in the hybrid upon reduction definitively confirms the cation insertion mechanism in these hybrids.

We can compare our results with previously reported COPs that have been doped with bulky organic anions and polyanions in order to correct their anion-insertion behavior into cation insertion (reported values of specific charge in A·h/kg are given in parentheses): e.g., PAni with poly(styrene-4-sulfonic-acid) (20),[41] PAni/thiocarbamato (46),[10] PAni/2-aminothiofenol (30).[10]

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(41) Morita, M.; Miyasaki, S.; Tanoue, H.; Ishikawa, M.; Matsuda, Y. *J. Electrochem. Soc.* **1994**, *141*, 1409.

It must be noted that contrary to the hybrid PAni/PMo12 all those systems make use of nonelectroactive anions that contribute to the mass of the polymer but not to the electrochemical activity. On the other hand, molecular adducts between COPs and other electroactive organic compounds such as organodisulfide and other sulfur species have also been studied as cathodes for lithium batteries.[10,18,19,21,22,42,43] Among these, high specific charge values between 152 and 233 A·h/kg have been reported for a PAni/2,5-dimercapto-1,3,4-thiodiazole cathode material.[21,22,43,44] Presently the hybrid PAni/PMo12 does not improve upon the best of these results although it is better than most of the PAni/polysulfonate systems mentioned above. The modest value of specific charge that we obtain is in part due to anticipated factors such as the relatively heavy Mo atoms involved but also to a reduced number of electrons exchanged per Mo within the range of stability of the hybrid. Furthermore, the cyclability of this particular system needs to be improved by optimizing the microstructure of the hybrid and the organic electrolyte. On the other hand, we consider the title hybrid electrode as the initial step for future research on hybrid materials with inorganic electroactive species anchored in the polymer matrix. It represents a valuable model of how to put molecular species to work in extended solid materials with useful physicochemical properties.

Conclusions

We have accomplished the chemical synthesis of a new hybrid material based of PAni and PMo12 cluster anion that can work as an insertion cathode. We have also obtained thin films of the same material electrochemically. Up to now this kind of synthesis had been performed by using additional oxidants. We have prepared the material using only $H_3[PMo_{12}O_{40}]$, which acts simultaneously as an acid, oxidizing agent, and source of doping anions. Molecular oxygen in air acts as a sacrificial oxidizing agent in this reaction. The PMo12 anion is anchored within the bulk of the polymer and becomes an integral part of the hybrid material. This is in contrast to smaller, more mobile doping anions that have been shown to get deinserted upon reduction. The retention of PMo12 in the polymer matrix must be due to its large size and high charge, resulting in negligible diffusion through the polymer network. True anchoring of PMo12 can be ensured even at relatively low potential reduction values. When the discharge is carried out below −0.4 V (vs Ag/AgCl), one can detect minor amounts of PMo12 in the electrolyte solution after reduction. Nevertheless, this is due either to superficial decomposition of the polymer matrix or to the release of entrapped oligomers upon reduction and not to deintercalation of the PMo12 from the polymer matrix.

We have shown how the anchoring of PMo12 within the material leads to insertion and deinsertion of cations for charge compensation during reduction and oxidation, respectively. This in turn represents a key modification of the cycling mechanism of polymeric electrodes which takes place with deinsertion/insertion of anions.

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Supporting Information Available: Figure S1: schematic diagram of the metacrylate container used for setting up reversible lithium cells with three electrodes (1 page). Ordering information is given on any current masthead page.

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(43) Sotomura, T.; Tasuma, T.; Oyama, N. *J. Electrochem. Soc.* **1996**, *142*.

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