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Integration of Hexacyanoferrate as an Active Species in a Molecular Hybrid Material. Transport Properties and Application of Polyaniline/Hexacyanoferrate as a Cathode in Rechargeable Lithium Batteries

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The hybrid organic−inorganic material formed by polyaniline and the hexacyanoferrate anion (PAni/HCF) constitutes a molecular hybrid where the anchoring of the electroactive anion within the polymer leads to its application as a functional material that harnesses the activity of the molecular species. Transport measurements of the hybrid have been carried out, both by cyclic voltammetry at different scan rates and ac impedance spectroscopy. An apparent diffusion coefficient of 5×10^{-8} cm^2/s and an activation energy of 15.5 kJ/mol (0.16 eV) have been obtained. The particular application of these hybrids to energy storage is shown here through their use as cathodes in lithium rechargeable cells. In this respect, the PAni/HCF hybrids show very good cyclabilities and high specific charges of up to 140 A·h/kg, unprecedented for this type of hybrid materials.

Introduction

The hybrid approach in materials science aims at the development of new materials based on the combination of organic and inorganic species in an attempt to obtain some reinforcement or synergy between them.[1]

Initially, the field was driven by the search for improved structural materials based on organic−inorganic polymers where silicon and carbon would share the spotlight.[2−4] But soon it was evident that the hybrid approach could also provide an innovative route for the development of novel and interesting functional materials, where chemical and electrochemical activity as well as optical or magnetic properties would be the main focus of interest, in addition to mechanical properties.[1]

Among the many possible categories of organic components, conducting organic polymers (COPs) constitute a very particular and interesting group due to their unique combination of conducting, electroactive, and polymeric properties. In our laboratory we have focused on the development of hybrid functional materials based on conducting organic polymers and various electroactive and photoactive inorganic species,[5] both molecular[6−13] or extended[14−17] in nature. In particular, we have been interested in the design of hybrid electroactive materials that could be used as insertion electrodes in rechargeable polymeric lithium batteries. In the case of hybrids formed by conducting organic polymers and oxide materials, such as PAni/V_2O_5,[14] both components could actually be used separately as electrode materials. This is not the case though for molecular hybrids such as the title compound where molecular species (otherwise commonly soluble) are anchored within the network of a COP to yield new materials with additional activity. Molecular species such as polyoxometalates[6−9] or hexacyanoferrate[10−13] whose zero-dimensionality and solubility would prevent their use can thus be used as active materials in solid electrodes.

The title material, the hybrid formed by anchoring hexacyanoferrate anions (HCF) into polyaniline (PAni) is the latest of our molecular hybrids. Previously, we studied other molecular hybrids including PPy/polyoxometalate[6,7] and PAni/polyoxometalate[7,8] as models of hybrids with conducting organic polymers and oxide

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clusters, and PPy/HCF,[10,12] which showed a moderate charge capacity. On the other hand, the title PAni/HCF hybrid has shown very promising electrochemical properties as an insertion electrode, which have been recently communicated.[13] We report here a full account of its synthesis, electrochemical and transport properties, and its performance in reversible lithium cells.

Experimental Section

Reagents. Aniline (Aldrich, 99.5%) was distilled and stored in the dark under nitrogen at 4 °C. Other reagents were used as received.

Synthesis of PAni/HCF Hybrid. Twenty-five milliliters of 2.1 M $HClO_4$ solution (52.5 mmol) was added to 5.679 g of $K_3[Fe(CN)_6]$ (17.25 mmol) dissolved in 25 mL of water. The white precipitate obtained was filtered off and the yellow solution was added dropwise to 25 mL of a 0.2 M aniline solution kept at 0 °C. This mixture was stirred for 3 days while kept between 0 and 4 °C. (For comparison, samples synthesized at room temperature were also prepared). The black-green powder obtained was washed with water and then with ethanol and dried under vacuum at least for 12 h.

Electrochemical Studies and Batteries Analyses. Compact reversible electrochemical cells were set up in Swagelok test cells, using a Labconco 50700 glovebox, allowing for water and oxygen removal to less than 1 and 5 ppm, respectively. Li foil (16−13-mm diameter and 0.1-mm thick) was used as the negative electrode and a solution of 1 M $LiPF_6$ in 1:1 EC/DEC or EC/DMC was used as the electrolyte (soaking a fiberglass disk used as a separator between the anode and cathode). The cathode was a film made by mixing the PAni/HCF hybrids and Super P carbon and polyvinylidene fluoride (PVDF) (used as a binder) in acetone and subsequent evaporation of the solvent at room temperature. The cells were tested with charge/discharge cycles performed with an ARBIN model BT2042 potentiostat. The cycling method used was a galvanostatic charge and discharge between two voltage limits. The discharge regimes have been C/15, C/5, or C/1. Electrochemical studies were carried out with a computer-controlled EG&G PAR207A potentiostat/galvanostat.

HP 4192ALF impedance analyzer 5 Hz to 13 MHz or a Solartron Schlumberger 1250 frequency response analyzer with a Solartron Schlumberger 1286 electrochemical interface were used for the measurement of ac impedance. The frequency range studied was from 10^{-2} to 10^7 Hz. The samples were prepared as pressed pellets (1-cm diameter and 1.55-mm thick) by applying 0.5 ton pressure. In/Ga alloy (60/40% in weight) was used as a contact to the gold electrodes.

The electric resistivity of the pellets was measured by the Van der Pauw technique[18] with a HP 2432 multimeter. Samples of the materials were pressed into pellets at 10 ton onto which four copper leads were attached with silver paint.

Results and Discussion

Synthesis of the Hybrid. The synthesis of the title material deserves some discussion because it aims at the isolation of polyaniline with hexacyanoferrate as the exclusive doping anion. The oxidative polymerization of aniline to yield polyaniline takes place spontaneously in an acidic and oxidizing medium. Ferricyanide is sufficiently oxidizing to induce the polymerization. The use of any mineral acid to provide the protons needed for the isolation of the conducting polyemeraldine PAni would necessarily introduce additional anions, which could compete with hexacyanoferrate for the doping and insertion within the polymer. Therefore, our synthetic procedure includes a metathesis reaction to isolate the acidic derivative of hexacyanoferrate. This was accomplished by reaction of the potassium salt with $HClO_4$, and the resulting precipitate of $KClO_4$ was filtered off. Similar alternatives (use of an ion-exchange column or in situ precipitation of $KClO_4$ in a one-pot synthesis) have been tried previously with similar results for the synthesis of PPy/HCF hybrids.[10] The procedure reported here provides a way to prepare the title hybrid, with aniline-to-hexacyanoferrate ratios very close to the maximum attainable (6−8 aniline rings per hexacyanoferrate molecule for samples prepared at 0 °C; 8−9 for those prepared at room temperature) in a clean and quantitative manner that ensures the exclusive incorporation of hexacyanoferrate to the polymer matrix in high concentrations.

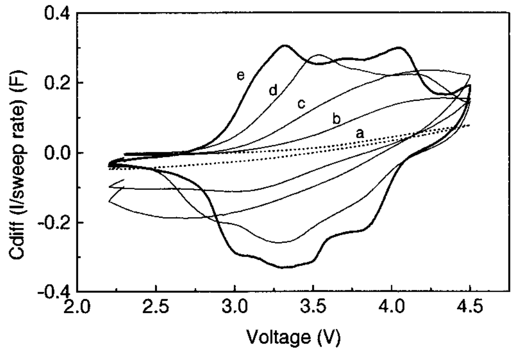

Figure 1. Cyclic voltammograms of PAni/hexacyanoferrate measured at several scan rates between 0.02 and 50 mV/s. Voltage range: 2.2−4.5 V. The current has been normalized with respect to scan rate. For clarity only 5 selected CVs are shown out of the 12 used to analyze the data shown in Figure 2. (Scan rates: $a = 20$ mV/s, $b = 10$ mV/s, $c = 2$ mV/s, $d = 1$ mV/s, and $e = 0.2$mV/s.)

Transport Properties. *1. Effective Diffusion Coefficient for the Hybrids Polyaniline/Hexacyanoferrate (PAni/HCF).* West et al. have described and applied elsewhere[19,20] a method to estimate an effective diffusion coefficient for ions inside a polymeric matrix from cyclic voltammograms recorded at slow enough sweep rates. Unlike measurements of ac impedance, where the potential applied to the cell is always the same, in this method a sweep of voltage is carried out, so there is a certain influence of the polyaniline structure on the value of the effective diffusion coefficient obtained.

Figure 1 shows cyclic voltammograms of cells with a lithium anode, a cathode of the PAni/HCF hybrid (thin film, as described above), and 1 M $LiPF_6$ in ethylene carbonate:diethoxyethane 1:1 as the electrolyte recorded at different sweep rates (between 0.02 and 50 mV/s). To facilitate the comparison of voltammograms at different scan rates, the curves are normalized as differential capacity curves. So C_{diff} is obtained as the coefficient between the measured current and the sweep rate.

An apparent diffusion coefficient (D) can be calculated according to the following equation,

$$D = \delta^2/\tau \tag{1}$$

where δ is the thickness of the film and τ a time constant obtained from

$$\tau = V_{\mathrm{w}}/\alpha_{\mathrm{crit}} \tag{2}$$

In eq 2, V_{w} is the potential window, obtained from the

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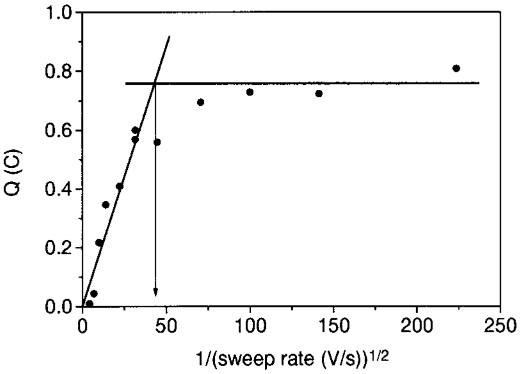

Figure 2. Plot of normalized specific charge vs scan rate from cyclic voltammetric data. From these data it is possible to extract the parameter α_{crit} (see text) from the intersection point to calculate the effective diffusion coefficient.

cyclic voltammetry, and α_{crit} is a critical sweep rate. The value of α_{crit} (V/s) is calculated from the intersection point of two lines with different slopes when the specific charge normalized with respect to sweep rate is plotted as a function of the inverse square root of the sweep rate (Figure 2).

From these calculations, if the thickness of the film is known (93 μm in our case), an effective diffusion coefficient of $D \approx 5 \times 10^{-8}$ cm^2/s is obtained for the PAni/HCF hybrid. It must be noted that this value is almost 2 orders of magnitude larger than that obtained by West and colleagues for other conducting polymers. Thus, for polypyrrole films an effective diffusion coefficient of $D = 10^{-10}$ cm^2/s was obtained[20] by the same method despite the fact that in that case the materials had been grown electrochemically as thin films. Our films of chemically synthesized hybrid present a faster diffusion most likely due to the different insertion mechanism taking place upon redox cycles. Thus, conventional conducting organic polymers such as the mentioned PPy material suffer oxidation processes with the insertion of anions, which can become de-inserted upon reduction. On the other hand, the insertion of hexacyanoferrate in our hybrid material takes place for good. The anion becomes anchored in the hybrid as has been previously shown for polyoxometalate anions[8,9] and for hexacyanoferrate itself in PPy/HCF hybrids in organic-solvent electrolytes[12] and therefore it is the available cations (Li^+ in our case) that become inserted and de-inserted upon reduction and oxidation, respectively. This modified mechanism explains the enhanced effective diffusion coefficient as well as the large energy storage capacity of the title hybrid, as presented below.

2. ac Impedance. ac impedance measurements were carried out to study the electrical behavior of the title material and the contribution of the grain boundary resistance. The pellets were only pressed, as the material cannot be sintered at high temperatures due to its limited thermal stability, and the contacts were made with In/Ga alloy. Gold electrodes were used. The conductivity was measured while cooling from room temperature (300 K) to 220 K using liquid nitrogen as the cryogenic agent. At temperatures below 220 K the resistivity of the sample was too high and led to the overloading of the measurement equipment and between 245 and 300 K inductive effects were observed.[21]

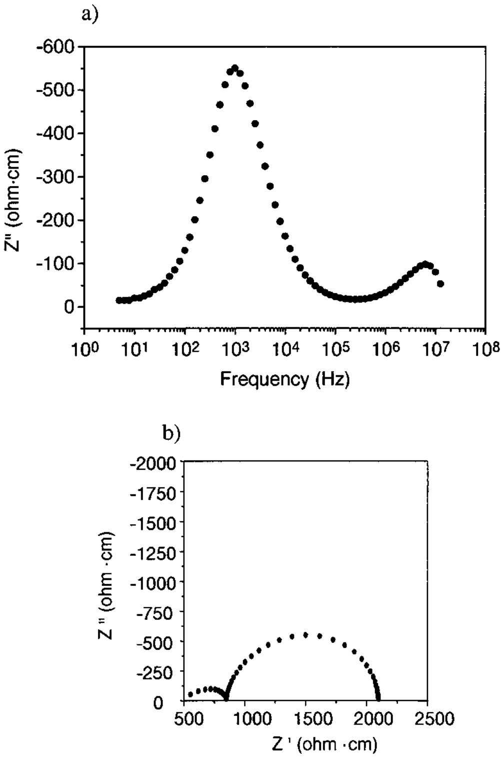

Figure 3. ac impedance data for PAni/HCF hybrid. (a) Bode–Bode plot. (b) Cole–Cole plot obtained for a sample at 238 K.

A typical set of ac data, in the form of complex impedance plane plot (Cole–Cole plot and Bode–Bode plot), is given in Figure 3.

For the analysis of these data we have applied the widely used model reviewed by Irvine, Sinclair, and West, which accounts for two major contributions to impedance, bulk, and grain boundary.[23] These plots and model allow one to distinguish between the electrical conductivity assigned to the intragrain (or bulk) and intergrain (or grain boundary) processes, taking advantage of the fact that each one dominates at different frequencies, resulting in separate semicircles for each kind of conduction (for a more detailed description, see refs 22 and 23). The low-frequency semicircle can be assigned to the grain boundary while the high-frequency one was associated with the intragrain or bulk response of the sample. The value of their capacitance, $C_{gb} = 60–200$ nF (grain boundary) and $C_b = 4–22$ pF (bulk), found from the maximum of each semicircle, using the relation $\omega RC = 1$, are consistent with this assignment.[23] The total resistance of the sample is determined predominantly by the grain boundary factor. A typical Arrehnius plot for the total and bulk conductivity is shown in Figure 4. Both sets of data are in very good agreement with Arrehnius law over the range of temperatures studied. From the slope of the linear fit for the bulk contribution the activation energy of this PAni/HCF

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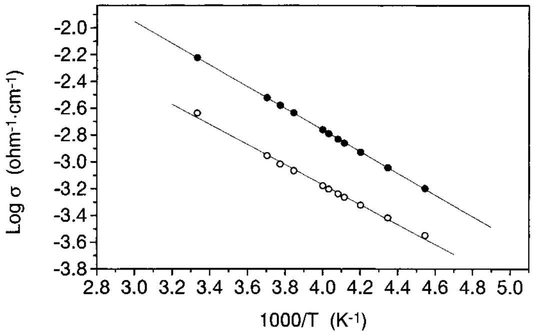

Figure 4. Arrhenius plot of the total (○) and intragrain (●) conductivity of PAni/HCF hybrid obtained by ac impedance measurements.

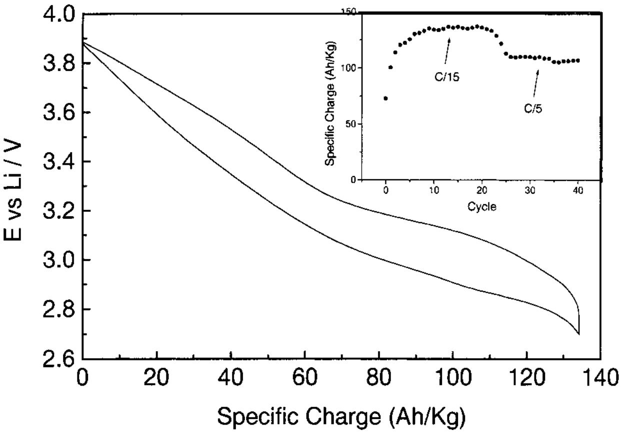

Figure 5. Charge–discharge cycle (10th) at a discharge rate of C/15 of a reversible lithium cell with PAni/HCF as active cathode material. Anode: lithium metal. Electrolyte: 1 M $LiPF_6$ in EC:DMC 1:1. The inset shows the evolution of specific charge upon cycling (at C/15 and then C/5 rates).

hybrid material is calculated, obtaining a value of 15.5 ± 0.6 kJ/mol (0.16 eV). This value is similar to the ones reported for other conducting polymers.[24–26]

Finally, dc conductivities of several samples of PAni/HCF were estimated using Van der Pauw's method.[18] The values obtained, ranging from 8×10^{-2} to 7×10^{-3} S/cm, are consistent with the values obtained from ac impedance measurements, which are, at 300 K, 2.3×10^{-3} S/cm (total conductivity) and 6×10^{-3} S/cm (bulk).

Battery Analyses. To be used as cathodes in lithium rechargeable batteries, the hybrids were mixed with PVDF as a binder (25% in weight) and Super P Carbon (15% in weight) to obtain films. These cathodes were tested in lithium batteries between 2.7 and 3.9 V (vs Li anodes), at different discharge regimes (C/15, C/5, C/1), using 1 M $LiPF_6$ in EC/DMC 1:1 as the electrolyte. The initial potential of such batteries were usually around 3.3 V (vs Li).

For most of the batteries studied, the values of the specific charge obtained were over 100 A·h/kg, maintaining their initial specific charge for more than 100 cycles with no significant decrease in its value, but specific charge values as high as 137 A·h/kg have been obtained at moderate discharge rates of C/15.

Table 1. Theoretical and Experimental Specific Charge Values for Different Molecular Organic–Inorganic Hybrids: Polypyrrole–Phosphomolybdate (PPi/PMo_{12}), Polyaniline–Phosphomolybdate ($PAni/PMo_{12}$), Polypyrrole–Hexacyanoferrate (PPi/HCF), and Polyaniline–Hexacyanoferrate (PAni/HCF)

hybrid material	theoretical specific charge (A·h/kg)	$n(e^-)^a$	experimental specific charge (A·h/kg)	reference
PPy/PMo_{12}	63	5.7	35	5
$PAni/PMo_{12}$	75	7.5	53	5,8
PPy/HCF	103	4	69	12
PAni/HCF	142	4	137	this work

[a] Number of electrons involved in the redox reaction (used to calculate theoretical specific charges).

These values are very close to the maximum theoretical specific charge expected for these hybrid materials, and are the best and more promising results obtained for molecular organic–inorganic hybrid materials reported up to now (see Table 1). Furthermore, the good cyclability shown by these cathode materials is the best proof of their stability upon cycling and the absence of chemical or electrochemical degradation.

A comparison of the title materials with transition metal oxides such as Li_xCoO_2 or $Li_xMn_2O_4$ presently used as active materials in the development of reversible lithium batteries is only partially relevant because those oxides constitute higher voltage materials for secondary systems and have been subject to many years of development and optimization, but it should be noted that the cells reported here with the hybrid PAni/HCF as active cathode material are able to reversibly cycle one electron per metal atom (equivalent in this case to 140 A·h/kg), which is a very good result when compared with the limited reversible insertion of 0.5–0.8 electrons per metal atom traditionally obtained from the oxide cathodes during their years of development.

Conclusions

The title hybrid material represents a good example of what can be accomplished with the hybrid approach in the field of functional materials. Generically, this approach brings together organic and inorganic components, each with distinctive properties and problems, and increasing their degree of interaction at a nanometric scale leads to the birth of new materials, hopefully with improved properties.

In the present case the hybrid approach reaches the chemical limit. Hexacyanoferrate is an electroactive inorganic complex molecule able to reversibly cycle one electron per metal atom. This compares favorably with many transition metal oxides commonly used as active materials in rechargeable lithium batteries, such as $LiCoO_2$ or $LiMn_2O_4$, which typically cycle reversibly less than one electron per metal atom. But as it stands, that complex could not be used as the basis for an electrodic material precisely because of its molecular nature and solubility. Its anchoring within the framework of a conducting organic polymer, as shown here, leads to a hybrid material that allows the harnessing of its electrochemical activity for the storage of charge in reversible lithium cells. The values of specific capacity obtained for this hybrid material (137 A·h/kg) show clearly that both the polymer and the complex contribute essentially their maximum electrochemical capacity

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to this task (140 A·h/kg corresponding to the cycling of 4 electrons per formula unit $\{(C_6H_5N)_6[Fe(CN)_6]\}_n$, i.e., one electron per hexacyanoferrate and 0.5 electrons per aniline ring). Furthermore, this material, with the polymeric nature and typical semiconducting behavior of conducting polymers, not only presents the added activity of the inorganic species but also exhibits improved ionic diffusion ($D = 5 \times 10^{-8}$ cm^2/s) due to the cation-insertion mechanism, which constitutes another characteristic advantage of these hybrid materials, in this case with respect to purely organic conducting polymers.

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