Triple hybrid materials: A novel concept within the field of organic–inorganic hybrids

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Abstract

We explored a new approach within the field of hybrid materials, namely, an integration of an electroactive inorganic molecule into a conducting polymer that in turn is intercalated into an extended inorganic oxide. In particular we present the specific material formed by hexacyanoferrate-doped polypyrrole or polyaniline inserted in turn into layered V_2O_5. This novel kind of hybrid with three components interacting at a molecular level is what we have called, triple hybrid materials (THM). The synthetic approach was based on our earlier work on PAni/V_2O_5, PAni/HCF and PPy/HCF systems. The materials obtained were characterized by FTIR, XRD, TGA, elemental analyses, and ICP. The electrochemical properties of THMs as insertion cathodes in rechargeable Li cells were also explored. The initial specific charge was high for PPy/HCF/V_2O_5 system (160 Ah kg^{-1}), giving a greater value than for their corresponding simple hybrids: PPy/HCF (69 Ah kg^{-1}) and PPy/V_2O_5 (120 Ah kg^{-1}). Repeated charge–discharge cycles showed a poor cyclability, which could be related to the voltage limit values during recharge, overoxidation of the polymer, or to the detrimental effect of structural water from THMs. Nevertheless, the present work showed a novel route towards a more complex and versatile electroactive hybrid design.

1. Introduction

Nowadays, hybrid materials based on organic and inorganic components represent a wide field of innovation within material science [1a]. Research on the topic of hybrid materials involves challenges and opportunities. The most important challenge is managing to synthesize hybrid combinations that keep or enhance the best properties of each of the components while eliminating or reducing their particular limitations. This challenge opens the opportunity to develop new materials with sinergistic behavior. Also, the hybrid approach is especially useful for combining organic and inorganic species with complementary properties and reactivities. This behavior can lead to improved performances or to the finding of new and useful properties [1].

The work in our group has been centered on a particularly fruitful and wide group of functional hybrid materials based on conducting organic polymers (COPs) as components. This category alone accounts for a large number of materials and applications [1b]. Their functionality, based on the electroactivity of their components, allows them to be used as electrodes for energy storage devices. These types of hybrid material have been classified into three groups depending on the type of matrix and guest phase: "OI" (organic–inorganic, molecular hybrids), "IO" (inorganic–organic, intercalation compounds), and "nanocomposite" materials [1b].

In this context we considered the possibility of triple hybrids with "nested" species inorganic (molecular)–organic (polymer)–inorganic (extended oxide) in which all the components would be electroactive, thus, aiming at higher energy storage capacities over wider potential ranges. In this paper we present the development of this idea in the form of a hexacyanoferrate (HCF)–COP–V_2O_5 combination. This triple hybrid material was constructed through the doping of a conducting polymer with $[Fe(CN)_6]^{3-}$ hexacyanoferrate (HCF), followed in some cases by the intercalation of the resulting O–I

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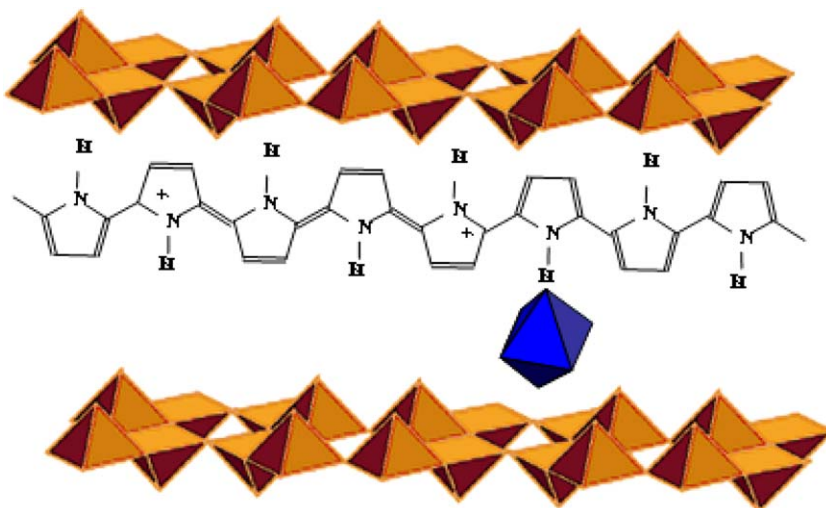(P. Gómez-Romero).

Fig. 1. Schematic diagram of the desired triple hybrid formed by a hexacyanoferrate-doped conducting polymer (polypyrrole in this case) intercalated into layered V_2O_5.

hybrid in between the layers of solid V_2O_5. Leading to what we call a I–O–I hybrid. Fig. 1 shows a schematic view of the desired structure for this triple hybrid.

It should be noted that this idea was also conceived and followed by other groups in quite different ways. Thus, simultaneously with our work, described below, the synthesis of similar triple hybrids was attempted through different procedures. Da Silva et al. [2] used a surfactant that was inserted between the layers of V_2O_5, then, according to the authors, HCF was immobilized on the surface of the hybrid instead of being intercalated. This work was essentially synthetic and only cyclic voltammetry was reported. On the other hand, the work carried out by Pokhodenko et al. [3] a double doping of polyaniline with phosphomolybdic acid, and *m*-cresol was reported. In contrast, our triple hybrid approach aimed from the beginning at the integration of all three electroactive species into a single bulk material in order to be used as Li insertion electrodes.

Earlier work carried out in our group concerning the PAni/HCF (OI) hybrid system showed that a stable good specific charge value was obtained for this molecular hybrid when used as a cathode material in lithium rechargeable cells (137 Ah kg^{-1} at *C*/15, 110 Ah kg^{-1} at *C*/5 charge–discharge rates) [4]. In contrast, the PPy/HCF hybrid system was also studied, but resulted only in moderated specific charge values, due to the formation of oxygenated groups (carbonyl, hydroxyl) on the polypyrrole chain [5,6]. With the triple hybrid approach we are trying to improve upon the performance of those binary hybrids (PAni/HCF, PPy/HCF).

We will describe here our syntheses of novel triple hybrid materials with polyaniline (PAni) or polypyrrole (PPy), doped with HCF and presumably its intercalation between the layers of V_2O_5. These syntheses were generally carried out in one-pot reactions and the resulting materials characterized by FTIR, XRD, TGA, elemental analyses, ICP, and finally tested in compact rechargeable lithium cells.

2. Experimental

2.1. Reagents

Pyrrole and aniline were purchased from Aldrich, distilled under reduced pressure, and kept under nitrogen at 4 °C. HClO$_4$ (70%) from Panreac and potassium ferricyanide K$_3$Fe(CN)$_6$·3H$_2$O 99% from Aldrich were used according to product specifications. For the synthesis of vanadium pentoxide gel we used a Dowex 50wx2-100 resin and sodium metavanadate 90% from Aldrich without further purification.

For the assembly of rechargeable lithium cells, metallic lithium ribbon (99.9%, 0.38 mm thick) from Aldrich was used as anode, a commercial product from Merck (Selectipur) composed of 1 M LiPF$_6$ in EC:DMC = 1:1 as electrolyte, and fiberglass membranes from Whatman GF/D dried at 100 °C for 48 h as electrode separators. All these components were kept in a dry box under argon for the assembly of the cells.

2.2. Characterization

Elemental analyses were systematically carried out to determine the percentages of C, N, and H in the hybrids (organic part), using an elemental analyzer Carlo Erba CHN EA 1108 at maximum combustion temperature of 1800 °C. ICP (inductively coupled plasma) analyses of vanadium and iron were carried out using a Thermo Jarrell-Ash model 61E Polyscan multichannel apparatus. TGA analyses were carried out under argon with a heating rate of 2 °C min^{-1} up to 360 °C and keeping this temperature for 6 h on a Perkin Elmer ATG-7 thermobalance. FTIR spectroscopy was carried out on pellets of the samples dispersed in dry KBr, using a Nicolet 710 FTIR spectrophotometer or a Perkin Elmer Spectrum one. Powder XRD analyses were carried out in a Rigaku with rotating anode, model "Rotaflex" Ru-200B with a secondary graphite monochromator with a Cu Kα radiation (λ = 1.5418 Å).

The electrochemical studies in lithium rechargeable cells were carried out in swagelok cells using an ARBIN potenciostat–galvanostat model BT2042. The triple hybrid materials were used as cathodes in composite powder versus metallic lithium anodes, by thoroughly mixing with 30% weight of super-P carbon. The charge–discharge of the cells was performed between a voltage range of 3.8 and 2.1 V with a slow rate of $C/40$.

3. Results and discussion

3.1. Synthesis

The synthesis of PPy/HCF/V_2O_5 and PAni/HCF/V_2O_5 triple hybrids were carried out by means of an oxidative polymerization of the monomer (aniline or pyrrole), in the presence of $H_3Fe(CN)_6$ and V_2O_5 gel solutions. The two inorganic reagents oxidize aniline or pyrrole to get incorporated to the hybrid compensating at the same time the positive charge of the conducting polymer. Table 1 shows the molar ratio used for the synthesis of each polypyrrole (PPy) and polyaniline (PAni) triple hybrid syntheses. The ferricyanide acid derivative $H_3Fe(CN)_6$ was freshly prepared by a metathesis reaction between potassium ferricyanide ($K_3Fe(CN)_6$) solution (40 ml) and $HClO_4$ (see Table 1 for the used amounts), with precipitation of $KClO_4$, which was filtered off resulting in the acidic $H_3[Fe(CN)_6]$ solution that was risen to a volume of 50 ml. On the other hand, V_2O_5 gel was prepared as described by Livage [7], aged for 3 months previously to their use, titrated to determine the precise amount of V(V) [8], and then the desired amounts of V_2O_5 were diluted with deionized water to complete a 50 ml solution.

For the case of PPy/HCF/V_2O_5 hybrids the syntheses were carried out as follows: the acidic HCF solution was placed in an ice bath with magnetic stirring (500 rpm), V_2O_5 solution (V_2O_5 gel diluted in deionized water) was added in 3 min, then 50 ml of a 0.072 M pyrrole solution was added in another 3 min, and after 30 min of reaction the solid formed was filtered off, washed with deionized water until no coloration came through, and finally collected and dried under vacuum for 3 days.

The synthesis of the triple hybrid with PAni was carried out similarly but using a 0.22 M aniline solution (50 ml) with an extended reaction time of 120 h.

Table 1
Molar ratio used in the synthesis of each polypyrrole triple hybrid samples

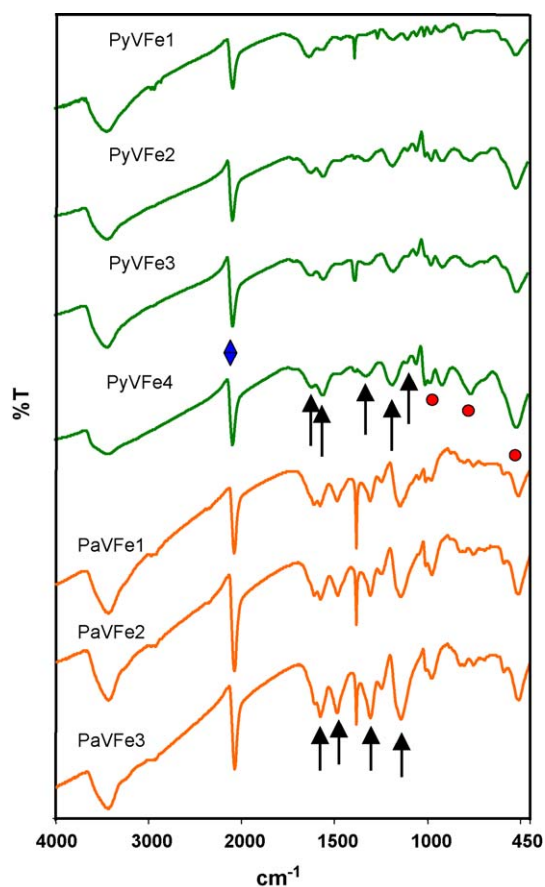| Sample	Molar ratio (monomer:V:Fe)	$K_3[Fe(CN)_6]$ + $HClO_4$	Excess reagent
PyVFe1	(0.5:1:1)	2.37 g + 1 ml	Double amount of inorganics
PyVFe2	(0.5:0.5:0.5)	1.18 g + 0.5 ml	Normal
PyVFe3	(0.5:0.5:1)	2.37 g + 1 ml	HCF excess
PyVFe4	(0.5:1:0.5)	1.18 g + 0.5 ml	V_2O_5 excess
PaVFe1	(3:0.5:0.5)	0.602 g + 0.2 ml	Normal
PaVFe2	(3:1:0.5)	0.602 g + 0.2 ml	V_2O_5 excess
PaVFe3	(3:0.5:1)	1.205 g + 0.4 ml	HCF excess

Fig. 2. FTIR spectra of all our PPy and PAni triple hybrids. Vibrational modes of V_2O_5 are marked with circles, the most characteristic peak of HCF marked with a diamond (2079 cm^{-1}, C≡N stretching), and the ones assigned to PPy or PAni (see text) with arrows.

3.2. Basic characterization

In this section, we describe the different analyses used to determine the presence of the three components in the triple hybrid, the stoichiometry, and the calculation of the formula weight.

In Fig. 2 we show the FTIR spectra of all our PPy and PAni triple hybrids, where we have detected the three components in every sample. We detected the vibrational modes of V_2O_5 marked with circles (515 and 757–760 cm^{-1} for V–O–V vibrational modes, and at 973–981 cm^{-1} for V=O stretchings), the most characteristic mode of HCF marked with a diamond (2079 cm^{-1}, C≡N stretching), and the ones belonging to the formation of PPy (1053 cm^{-1} inner C–H plane and C–N, 1179 cm^{-1} ring vibration, 1382 cm^{-1} ring vibration C=C/C–C and C–N contributions, and 1555 cm^{-1} C=C/C–C modes) or PAni (1147 cm^{-1} C–H ring vibrations, 1310 cm^{-1} C–N of arylic secondary amine, 1486 and 1580 cm^{-1} to benzenic/quinone ring deformation) with arrows. In the case of hybrids with PPy we observed in almost all samples (PyVFe2, PyVFe3, and PyVFe4) a very weak band around 1700 cm^{-1} which was associated to C=O formation, indicating some overoxidation of PPy [9].

XRD patterns of triple hybrid samples with PPy and PAni are shown in Figs. 3 and 4, respectively. We must point out that
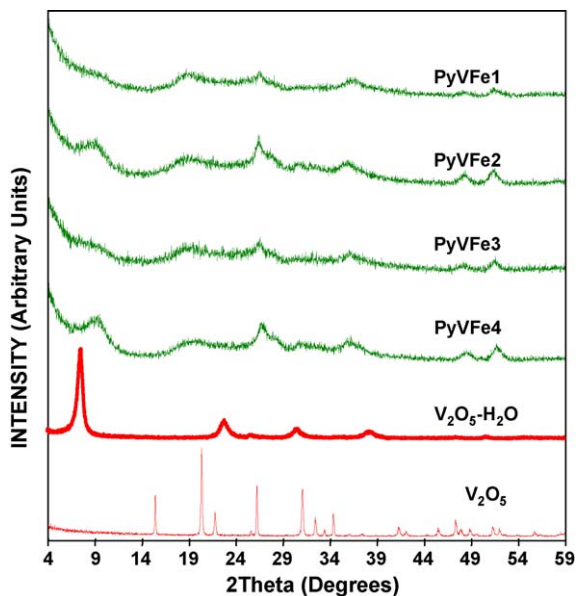
Fig. 3. X-ray diffraction patterns of PPy triple hybrids and of V_2O_5 with (V_2O_5–H_2O) and without (V_2O_5, crystalline) intercalated water for comparison.

previously studied hybrids based on HCF anchored to PPy and PAni did not reveal any diffraction peaks in the XRD patterns, indicating an amorphous phase for these simple hybrids [9]. In the case of THMs, XRD patterns revealed some wide diffraction peaks characteristic of a poorly crystalline structure, almost amorphous, due to the polymer. On the other hand, the characteristic 0 0 1 peak of the diffraction pattern of layered V_2O_5 structure present at low angles indicated the spacing between its layers. This 0 0 1 spacing was usually 11.5 Å ($2\theta = 7.68°$) when one equivalent of water (2.8 Å) was intercalated (see Fig. 3, XRD pattern of V_2O_5 with and without intercalated water), and 4.27 Å ($2\theta = 20.3°$) when in its crystalline form (without interlayer water). For the case of the triple hybrids with PPy, samples PyVFe2 and PyVFe4 showed a peak at low angles (ca.
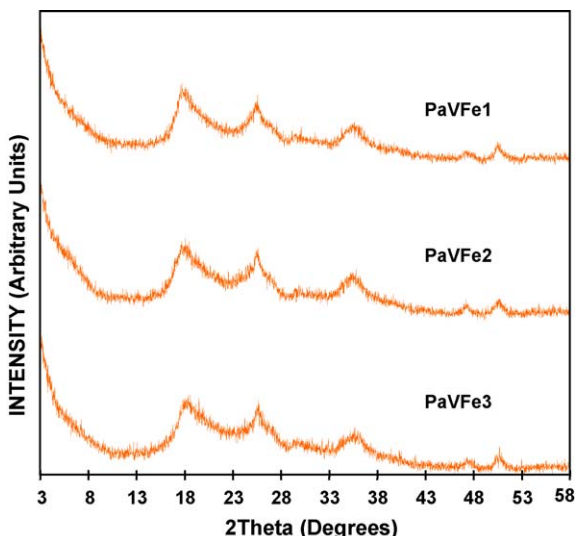
$2\theta = 8.0°$ and $8.26°$, respectively) corresponding to a spacing of 11.0 and 10.7 Å, respectively, while in the other two samples (PyVFe1 and PyVFe3) only a shoulder could be detected at ca. $8.0°$. This spacing belongs to the 0 0 1 diffraction peak of V_2O_5, indicating a smaller particle size of V_2O_5 in these PPy triple hybrid samples. The net gap between V_2O_5 slabs in samples PyVFe2 and PyVFe4 was determined to be 2.3 and 2.0 Å, respectively, indicating that no PPy was intercalated (expected expansion of 5.3 Å), nor HCF anion (expected 4 Å), but instead only water molecules as in V_2O_5 xerogels (pattern inserted in Fig. 3, V_2O_5–H_2O). However, PPy and HCF are unambiguously present in the hybrid as indicated by FTIR. Nevertheless, HCF results water-insoluble when anchored to PPy, which suggested the isolation of the PPy/HCF hybrid which was segregated from the V_2O_5 interlayer spacing and probably covering the V_2O_5 particles.

On the other hand, we could not observe any apparent peak at low angles related to an intercalation in V_2O_5 for triple hybrids with PAni. However, a weak shoulder around $5°$, hardly distinguishable from the background, was seen though somewhat more clearly detected in the sample PaVFe2, which hints at the presence of a spacing of ca. 17.6 Å for this hybrid. Therefore, estimating the spacing for the desired triple hybrid structure (Fig. 1), where PPy (5.3 Å) or PAni (5.5 Å [10]) is doped with HCF (4 Å) and inserted between the layers of V_2O_5, the spacing results in 18 Å ($2\theta = 4.9°$) or 18.2 Å ($2\theta = 4.9°$) respectively if the expansions were additive. These materials were very poorly crystalline, as for the case of the PPy hybrids above, even 0 0 1 peaks, normally stronger in V_2O_5 xerogels, were very weak (wider) indicating a smaller particle size of V_2O_5 in the triple hybrids. For the case of all triple hybrid samples with Ppy, a shoulder peak obscured by the strong signal of the direct X-ray beam was present at lower angles, suggesting that we cannot rule out the existence of a wider expansion between the layers of V_2O_5 and a probable formation of the triple hybrid structure even in the case of PPy hybrids. On the other hand, with all due precautions in view of the very poorly defined shoulder in hybrids with PAni, the agreement between our calculation (18.2 Å, $2\theta = 4.9°$) and the position of the shoulder (17.6 Å, $2\theta = 5°$) is an indication of a hybrid material with very poor crystalline but with both PAni and HCF components inserted within the V_2O_5. Nevertheless, our XRD data will obviously need confirmation by other techniques.

TGA analyses were carried out to determine the amount of inorganic and organic matter plus hydration water in our samples. In Figs. 5 and 6 we show the TGA analyses carried out for all our triple PPy and PAni hybrid samples, respectively. There are two important weight losses that are easily observed in the derivative curves (inset). The first loss takes place between 70 and 80 °C for PPy hybrids and 55 °C for PAni hybrids, corresponding to loosely bound hydration water. A second main loss takes place during the isothermal heating at 360 °C, corresponding to the combustion of the polymer. The remaining weight percentage corresponds to the inorganic part of the hybrid (HCF + V_2O_5), and turned out to be similar for all PPy hybrid samples (69.5% for PyVFe1, 69.0% for PyVFe2, 68.9% for PyVFe3, and slightly higher for PyVFe4 with a 73.7%), and
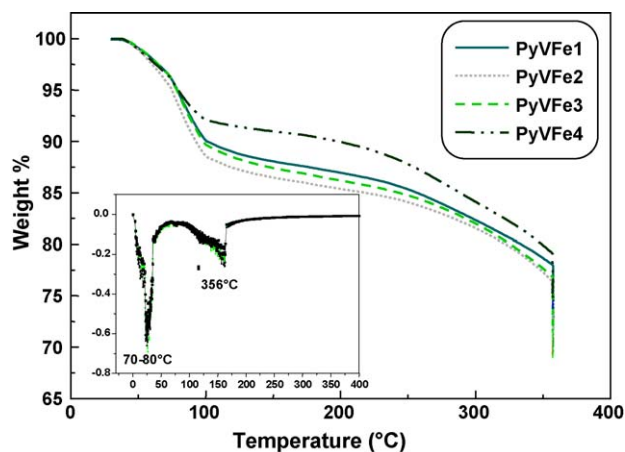

Fig. 4. X-ray diffraction patterns of PAni triple hybrid Materials.

Fig. 5. Thermogravimetric analyses (TGA) for triple hybrids based on polypyrrole.

Fig. 7. Initial discharge and first recharge cycle of Li rechargeable cell assembled with triple hybrids HCF–PPy–V_2O_5 as cathodic material at a slow rate (C/40).

PAni hybrids (71.78% for PaVFe1, 73.09% for PaVFe2, and 75.84% for PaVFe3). The stoichiometries of these THMs were calculated based on elemental analyses, TGA analyses, and ICP analyses. In Table 2 we present the summarized data of these experimental analyses and the calculated values for the proposed stoichiometric formulas. As we can observe in Table 2, all THMs stoichiometries revealed a great amount of water, indicating the need for a better drying procedure.

3.3. Electrochemical characterization

The electrochemical characterization was carried out using the triple hybrid composite powder samples as cathodes in rechargeable lithium cells (see Section 2). In Figs. 7 and 8 we show the first charge/discharge cycle for every Li cell tested. For the case of cells with PPy triple hybrids as cathodes, we obtained high specific charges, between 125 and 160 Ah kg^{-1}. When PAni triple hybrid samples were used as cathodes, specific charges between 89 and 124 Ah kg^{-1} were obtained. The
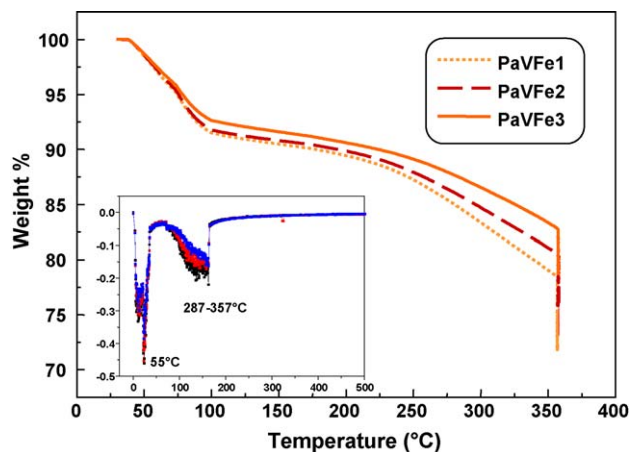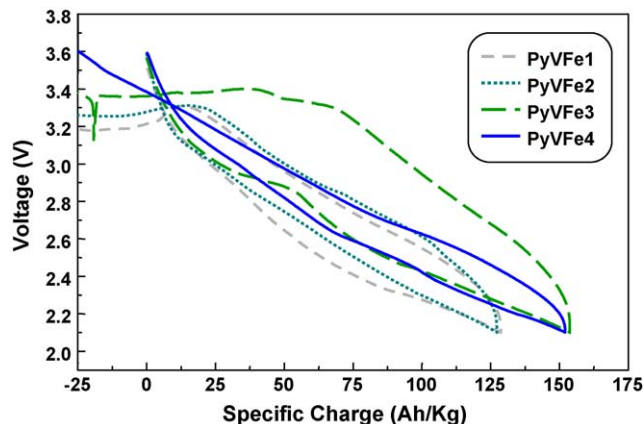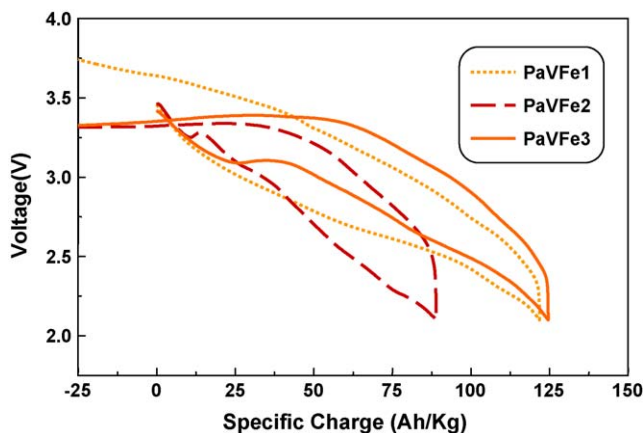

Fig. 6. Thermogravimetric analyses (TGA) for triple hybrids based on polyaniline.

Table 2
Summarized data of the chemical analysis to determine the respective stoichiometry of each PPy and PAni triple hybrid samples

	Monomer:V:Fe	% C	% N	% H	% V	% Fe	Formula	Sample
Experimental	(0.5:1:1)	17.03	13.14	2.02	24.93	7.40	$(C_4H_2N)_{0.64}V_2O_5[HCF]_{0.53}3.8H_2O$	PyVFe1
Calculated		17.05	13.23	2.37	25.19	7.32	FW = 404.3	
Experimental	(0.5:0.5:0.5)	10.45	7.23	1.38	19.01	3.77	$(C_4H_2N)_{0.60}V_2O_5[HCF]_{0.35}10H_2O$	PyVFe2
Calculated		11.18	7.68	4.54	21.65	3.91	FW = 470.4	
Experimental	(0.5:0.5:1)	17.56	12.27	2.13	24.92	6.55	$(C_4H_2N)_{0.76}V_2O_5[HCF]_{0.47}4H_2O$	PyVFe3
Calculated		17.46	12.44	2.57	25.28	6.51	FW = 403.0	
Experimental	(0.5:1:0.5)	12.35	8.57	1.62	32.28	4.80	$(C_4H_2N)_{0.43}V_2O_5[HCF]_{0.25}2.8H_2O$	PyVFe4
Calculated		12.34	8.62	2.21	32.52	4.45	FW = 313.3	
Experimental	(3:0.5:0.5)	33.50	14.68	2.54	17.84	6.79	$C_6H_4N(V_2O_5)_{0.48}[HCF]_{0.33}1.3H_2O$	PaVFe1
Calculated		35.39	15.41	2.45	18.06	6.80	FW = 270.77	
Experimental	(3:1:0.5)	28.17	14.86	2.31	19.87	7.46	$C_6H_4N(V_2O_5)_{0.75}[HCF]_{0.52}2.7H_2O$	PaVFe2
Calculated		28.42	14.97	2.45	19.82	7.53	FW = 385.37	
Experimental	(3:0.5:1)	35.22	15.03	2.61	16.66	6.73	$C_6H_4N(V_2O_5)_{0.42}[HCF]_{0.31}1.4H_2O$	PaVFe3
Calculated		36.67	15.56	2.66	16.62	6.72	FW = 257.42	

Fig. 8. Initial charge–discharge cycle of Li rechargeable cell assembled with triple hybrids HCF–PAni–V_2O_5 as cathodic material using a slow rate (C/40).

expected theoretical values (calculated for $0.33e^-$ per pyrrole ring or for $0.55e-$ per aniline ring, $2e^-$ per V_2O_5 (one per V atom) and $1e^-$ per Fe atom) were between 160 and 200 Ah kg^{-1} for the different compositions of PPy triple hybrids, and between 172 and 176 Ah kg^{-1} for PAni triple hybrids. These theoretical values differed from the experimental initial specific charge values by 20% for PPy hybrids, and by 40% for PAni hybrids, suggesting an enhanced contribution of each component in the PPy triple hybrid to the total specific charge value in comparison with the PAni systems. Also, we must point out that THMs based on PPy gave higher specific charge values compared with their correspondent simple hybrids: PPy/HCF (69 Ah kg^{-1}) and PPy/V_2O_5 (120 Ah kg^{-1}) [9]. Furthermore, we must emphasize that the voltage could not reach the 3.8 V set for recharge in all cases, causing a detrimental effect on the cyclability. A common reason for this kind of behavior is the existence of ongoing catalytic oxidation processes, normally on organic solvents, although in our case could also be due to the large amount of structural water from the THMs (see Table 2). On the other hand, in the specific case of the PPy triple hybrid, we cannot rule out an additional detrimental effect due to the formation of C=O groups during synthesis as explained above. These two factors (structural water and C=O groups) will need to be sorted out in future studies.

4. Conclusions

We carried out the syntheses of two series of PPy/HCF/V_2O_5 and PAni/HCF/V_2O_5 triple hybrids, confirming by FTIR and chemical analyses, the presence of all three components in the resulting materials. XRD patterns presented a shoulder in some samples at $2\theta = 4$–$5°$, which suggested a wider expansion between the layers of V_2O_5 (of an otherwise very poorly crystalline material) adequate to accommodate both HCF and the conducting polymers between the V_2O_5 layers. All these analyses indicated the formation of a new type of hybrid material in which hexacyanoferrate dopes the conducting polymer and is dispersed at a molecular level in V_2O_5 particles or both are co-intercalated into an extended V_2O_5 phase. Concerning

the electrochemical performance of the novel PPy/HCF/V_2O_5 triple hybrid materials in lithium rechargeable cells, we obtained high initial specific charge values of 160 Ah kg^{-1}, giving a greater value than for a PPy/HCF system (69 Ah kg^{-1}), and a PPy/V_2O_5 system (120 Ah kg^{-1}) [11], which was not the case for PAni/HCF/V_2O_5 triple hybrid materials [4,12]. However, their cyclabilities were poor. This might have more to do with the choice of the voltage limit values during recharge and the structural water content in the THMs used as cathodes, since in all samples synthesized, the voltage could not reach the 3.8 V on recharge, or this could be due to the effect of C=O groups formed by overoxidation of PPy. Notwithstanding this uncertainty concerning the low cyclability, we would like to stress that this work constitutes an important precedent in relation to the synthetic chemistry of hybrid materials, since it is a first step in the design of novel approaches for functional hybrids of greater complexity, a field which should have important implications not only in energy storage applications, but also in the design of supported catalysts, optical and magnetic materials, sensors, etc.

Acknowledgements

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