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Improvement in the Ppy/V_2O_5 hybrid as a cathode material for Li ion batteries using PSA as an organic additive

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Abstract

With the aim of improving the electrochemical properties of this candidate cathodic material for lithium ion batteries, a vanadium oxide (V_2O_5) and polypyrrole (Ppy) hybrid was prepared using pyridinesulfonic acid (PSA) as additive. The hybrid synthesis has been carried out in the literature by chemical polymerization of pyrrole in the host inorganic matrix, using the V_2O_5 dispersed in an acidic solution as an oxidizing agent. In this work the hybrid has been synthesised with PSA giving good results compared to other samples of the pristine V_2O_5 and to the Ppy/V_2O_5 hybrid without additive. An improvement of about 20% in the charge storage capacity has been achieved. The reasons for this improvement are discussed and analyzed using different experimental techniques. The hybrid material has the added advantage of an improved performance without the addition of any binder or conducting element as a cathode in a lithium ion battery.

Keywords: Batteries; Li-ion; Cathode; V_2O_5; Conducting polymer; Hybrid material

1. Introduction

Recent research trends in the field of rechargeable lithium batteries are directed towards the development of cells with high specific energy (Wh kg^{-1}) and high energy density (Wh l^{-1}) [1]. The energy storage capacity in a rechargeable lithium or lithium-ion cell is mainly dependent on cathode materials. Cathodes formed from transition metal oxides demonstrate high specific capacity and high energy density [2–4]. When these materials are reduced/oxidized, Li^+ ions intercalate/deintercalate into the host matrix. The rate limiting step during the charging and discharging steps of these materials is often found to be the diffusion of Li^+ within the cathode. In addition, the electronic conductivity of these materials is usually quite low, increasing the ohmic drop [4]. On the other hand, special organic materials such as conducting polymers were also studied and proposed as candidates for the development of rechargeable plastic lithium batteries [5], but they also present some drawbacks such as low specific energy. In this context, hybrid organic–inorganic materials represent an opportunity to take advantage of the best properties of each type of material [6]. Hybrid electrodes for energy storage applications, with conducting polymers and a variety of active inorganic species have been prepared and studied, from molecular [7–9] to nanocluster [10–13] and extended inorganic phases [14,15] among which V_2O_5 stand out.

Vanadium oxide xerogel (V_2O_5) is one of the metal oxides frequently studied as cathode material. This compound exhibits a lamellar structure with V_2O_5 bilayers [16] constructed from VO5 square pyramids. The sheets are held together via weak bonding between the vanadium atoms and the oxygen from different pyramids of neighbouring layers [17,18]. The lithium intercalation occurs within these vanadium slabs. In order to improve the intercalation rate, and hence the capacity, vanadium oxide has been prepared as a xerogel with improved results. To prepare electrodes of V_2O_5 xerogel, a material with low viscosity and low electrical conductivity, the oxide powder needs to be mixed with a conducting matrix, such as carbon powder, and a binding material. In many cases, the use of a conducting

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polymer that can act as binding and conducting element has been proposed instead of adding electrochemically inactive materials.

Looking at the structure of V_2O_5, the space between layers is wide enough to introduce some organic compounds, such as conducting polymers [6,16]. The interactions can facilitate the formation of a hybrid material between the organic and inorganic (V_2O_5) compounds. The formation of hybrids of conducting polymers inserted in V_2O_5 takes place with the initial intercalation of the corresponding monomer molecules into the inorganic layered structure. The strong oxidizing character of the oxide induces the redox polymerization of the organic molecules. It is worth remarking that while the inserted polymer is partially oxidized during the process, the V_2O_5 itself suffers a partial reduction that renders it an electrically conductive mixed-valence (V^{IV}/V^{V}) oxide [6]. The hybrid material has higher electronic conductivity and lower crystallinity than the pristine V_2O_5 xerogel. These seem to be the reasons for the improvement on the charge–discharge behaviour.

Kanatzidis et al. started fundamental work on the hybrid synthesis in 1989 [19,20]. Many attempts have been made to use these V_2O_5/conducting polymer hybrid materials as a cathode in lithium-ion batteries. Since then, several authors have reported such composites in a number of studies [21–26]. Kuwabata et al. have studied Ppy/V_2O_5 composites formed by chemical polymerization of pyrrole using V_2O_5 powder dispersed in an acidic solution as oxidizing agent [27–29]. Following this methodology, simultaneous polymerization and precipitation of the hybrid material occurred. Good results were obtained, especially in the enhancement of charge–discharge capacity.

In order to further improve the electrochemical behaviour, the amount of intercalated Ppy seems to be an important parameter. The affinity of V_2O_5 for intercalating coordination compounds and organic ligands [30,31] is also widely known, especially nitrogenated ones [32,33]. As it is shown in the literature, these compounds can change the space between layers of V_2O_5 which can be helpful in the formation of the hybrid material, as it facilitates the monomer entry in the inorganic host. Moreover, the functional group of the intercalation compound and the intercalation mechanisms can change the structural and electronic behaviour of the resulting material. Therefore, if the intercalation compound can change the electric behaviour of the material, the charge storage capacity can be improved using nitrogenated organic compounds. In order to use an organic additive to enhance the electrochemical response, two main characteristics have been looked for: firstly, the additive must have a nitrogenated group in order to interact with the vanadium molecules and, thus, enable the layer separation in the molecular architecture. Finally, having a functional group that promotes the polymerization of the pyrrole molecules [34–36], as a sulfonic acid group, could be helpful to form a hybrid with good electrochemical behaviour. Pyridinesulfonic acid (PSA) has been chosen as an additive that fulfils these characteristics.

The objective of this article is to study the influence of the addition of pyridinesulfonic acid (PSA) to the Ppy/V_2O_5 hybrid and check the viability of this previous insertion step to improve the electrochemical behaviour.

2. Experimental methods

2.1. Materials and procedures

Experimental procedures used for the composite material synthesis are described below:

2.1.1. V_2O_5 gel

H_2SO_4 96% from Panreac $(NH_4)_2Fe(SO_4)_2\cdot 6H_2O$ 99.9% from Carlo Erba. $NaVO_3$ 99.5% and the ion-exchange resin DOWEX were purchased from Sigma.

Synthesis of the $V_2O_5\cdot H_2O$ gel was carried out by the cationic exchange method. Briefly, 4.5 g of sodium metavanadate ($NaVO_3$) were dissolved in water at 80 °C. Once cold the solution was passed through a cationic exchange resin DOWEX 2x-100. The initial colorless solution changed to yellow-orange corresponding to the formation of the metavanadic acid. The amount of V^{+5} in the $V_2O_5\cdot H_2O$ gel was analyzed by potentiometric titration method described elsewhere [37] with a CRISON pH meter with an Ag/AgCl electrode: 2 ml of V_2O_5 gel were dissolved in 30 ml of water and analyzed with $Fe(NH_4)_2(SO_4)_2\cdot 6H_2O$ (0.98 g in 100 ml of H_2O_4 0.25 M).

2.1.2. Ppy/V_2O_5 composite synthesis

A 12.5 ml of the V_2O_5 gel (0.036 M) were dissolved in 25 ml of deionized water. The solution was deaerated by bubbling N_2 through it for 10 min. After mixing under nitrogen atmosphere pyrrole (Py) was added dropwise until a Py/V_2O_5 molar ratio of 3/1 was reached. The dark red solution turned to black indicating the formation of Ppy/V_2O_5 composite. The reaction was kept for 20 min at room temperature. Then, the solid was filtered-off, washed repeatedly with water and dried under vacuum at room temperature.

2.1.3. Ppy/V_2O_5 composite synthesis in acidic solution

The composite synthesis in acidic solution was carried out in the same way as in the original synthesis, using a perchloric acid solution ($HClO_4$, 1 M) instead of ultrapure water. The use of acidic $HClO_4$ water solution as solvent gave a transparent yellow solution from the original cloudy and dense V_2O_5 xerogel solution.

2.1.4. PSA–Ppy/V_2O_5 composite synthesis

The composite synthesis with PSA as additive was carried out in the same way as the original synthesis, but adding in this case PSA 0.072 g in the V_2O_5 gel solution, previous to the Py addition (PSA/V_2O_5 molar ratio of 1/1) (Fig. 1).

2.2. Characterization techniques

2.2.1. XRD

X-ray powder diffraction data were collected using a Philips PW1710 diffractometer (Bragg–Brentano geometry; Cu Kα; graphite secondary monochromator; range 3–50° 2θ; step 0.025° 2θ; 1 s per step).

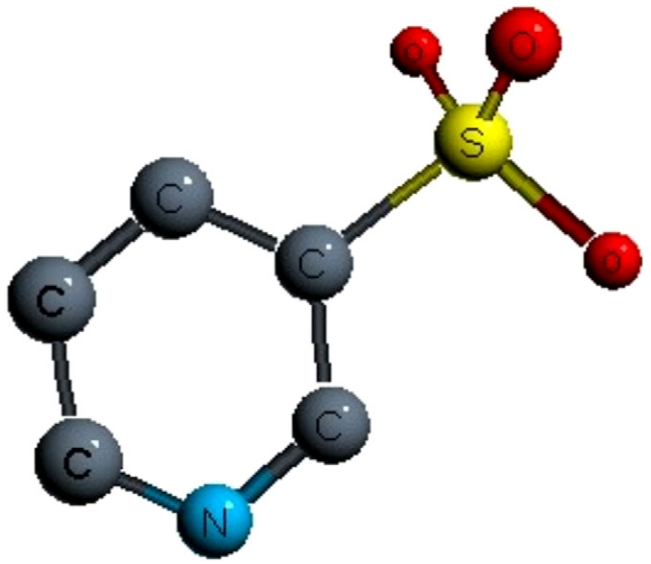

Fig. 1. Chemical structure of pyridinesulfonic acid (PSA).

2.2.2. *Elemental analysis*

Elemental analysis was carried out using a LECO-932 microanalyzer.

2.2.3. *FTIR*

Fourier transform infrared spectroscopy measurements were performed in a Fourier transform infrared NICOLET AVATAR 360 in absorption mode. All spectra were acquired in the range of 4000–400 cm^{-1} with a 2 cm^{-1} spectral resolution from compressed pellets of KBr and the hybrid materials.

2.2.4. *Electrochemical characterization*

Electrochemical studies of the final prototypes were performed with a Macpile-II potentiostat–galvanostat system under a constant current density in order to charge-discharge at *C*/40 in the 3.6–1.8 V range. Swagelok type cells were assembled in a glove box (LabMaster 130 MBraun). Lithium was used as negative electrode (anode) and they were cut in 8 mm diameter discs. A 5 mg of Ppy/V_2O_5 hybrid material was used as the positive electrode (cathode), by compressing against an aluminium current collector at 40 bar for 5 min. A solution of $LiPF_6$ in EC/DMC (50:50 in volume) (Merck) is used as electrolyte. The pure V_2O_5 electrode material was mixed with 10% of carbon as conducting material.

3. Results and discussion

The main characteristic pursued by the addition of the PSA was to improve the discharge capacity of the vanadium–polypyrrole hybrid electrode. The function of the additive would be to work as a molecular wedge increasing the interlayer space between layers for the insertion of monomers and at the same time, promoting a better polymerization of the monomers by the sulfonated group. Differences on the discharge capacity are shown in Fig. 2a. In this figure the discharge curves for the V_2O_5 xerogel (1), Ppy/V_2O_5 hybrid synthesised in acidic solution ($HClO_4$) (2) and PSA–Ppy/V_2O_5 (3) are compared. In Fig. 2b the discharge profile of the same V_2O_5 xerogel is plotted versus the hybrid material synthesised without acidic solution (4) and a Ppy electrode (5). These figures are used to analyse the influence of Ppy as conducting and binding element when the hybrid is synthesised using different conditions.

As can be seen in Fig. 2a, the intercalation of the conducting polymer (curves 2 and 3) improves the electrochemical response of the V_2O_5 (curve 1). These results demonstrate that the conducting polymer can act as binding and conducting element at the same time while contributing its electroactivity. Nevertheless, the best results are obtained using PSA as additive in the hybrid formation, obtaining an improvement of about 20% in

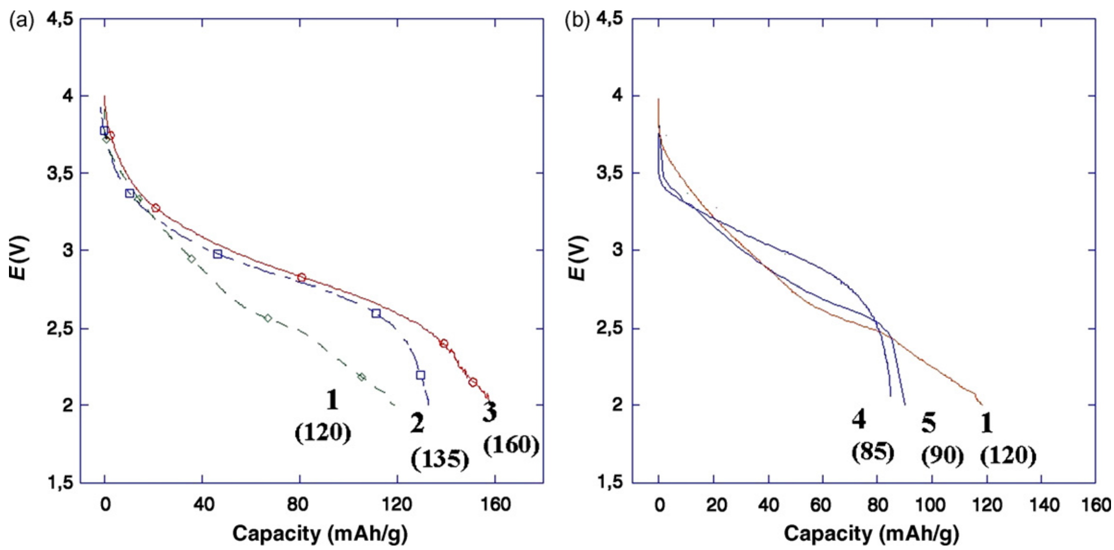

Fig. 2. (a) Discharge curves of as prepared: (1) pristine V_2O_5 with carbon black, (2) Ppy/V_2O_5 synthesised with acidic solution and (3) PSA–Ppy/V_2O_5. (b) First discharge curves of as prepared: (1) pristine V_2O_5, (4) Ppy/V_2O_5 synthesised without acidic solution and (5) Ppy electrode. Data were collected at *C*/40 discharge rate in 4–2 V range. Under parentheses values of discharge capacities in mAh g^{-1} are shown.

the charge storage capacity. Looking at the profile of the hybrid cathodes and pristine references, three different sections can be distinguished:

(a) *From 4 to 3.2 V versus Li*. While V_2O_5 (1), Ppy/V_2O_5 synthesised in acidic solution (2) and PSA–Ppy/V_2O_5 (3) have the same discharge profile, the profile of Ppy/V_2O_5 synthesised without acidic solution (4) is similar to the one of Ppy (5). These differences point out that while the initial discharge profile of hybrids 2 and 3 is dominated by V_2O_5, sample 5, without acidic solution, is governed by Ppy. It can be associated to the formation of non-homogeneous hybrid when no acidic solution is used and it will be analyzed below.

(b) *From 3.2 to 2.5 V versus Li*. In the case of Ppy/V_2O_5 (2, 4) and PSA–Ppy/V_2O_5 (3) the discharge profile is flatter than the one with V_2O_5 (1) or Ppy (5). When the cell voltage reaches 2.5 V the discharged capacity of the hybrid electrodes is greater than the one with V_2O_5. Besides, the potential of the hybrid materials during discharge is higher than that of the pristine V_2O_5 and Ppy electrodes. Therefore, combination at the nanosize level of active inorganic and organic components in a single material results in a hybrid with better electrochemical properties.

(c) *From 2.5 to 2 V versus Li*. The Ppy/V_2O_5 (2, 4) discharge profile falls rapidly, therefore the capacity does not increase too much. The V_2O_5 (1) profile becomes flatter in this range, and at the end of the discharge process, its final capacity is slightly lower than that of Ppy/V_2O_5. The profile of the PSA–Ppy/V_2O_5 (3) is similar to the V_2O_5, and flatter than the Ppy/V_2O_5, which results in an improvement in the capacity.

In Fig. 3 the cyclability of the hybrid synthesised with $HClO_4$ and PSA, the hybrid synthesised with $HClO_4$ without PSA and a hybrid synthesised without acid or PSA can be observed. As Fig. 3 shows, the influence of perchloric acid and PSA in the hybrid material is not only in the specific capacity of the material, but also the cyclability is improved. After 30 cycles, the capacity of the hybrid material synthesised with additive is around 130 mAh g^{-1} and 120 mAh g^{-1} with acid, while the hybrid synthesised without acid is down to 95 mAh g^{-1}.

These results are discussed below, supported by different experimental techniques. The enhancement of the discharge capacity and cyclability associated with the PSA addition to the Ppy/V_2O_5 hybrid is an important result and the role of the PSA has to be understood to continue improving the electrochemical behaviour of this electrode. With this aim XRD, FTIR and elemental analysis have been used to discern the influence of the PSA on the synthesis that increases the discharge capacity of the final hybrid.

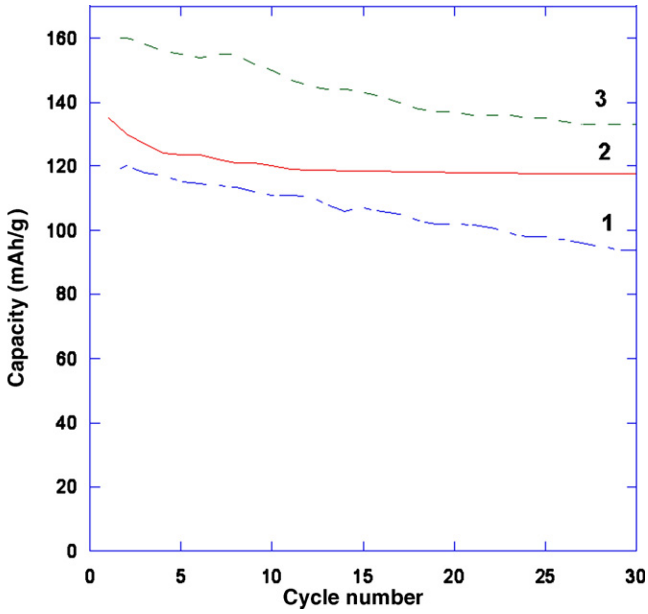

Fig. 3. Cyclability of the (1) Ppy/V_2O_5 hybrid synthesised without acidic solution and (2) in acidic solution $HClO_4$ without PSA, and (3) in acidic solution $HClO_4$ with PSA. Data were collected at *C*/40 discharge rate in 4–2 V range.

3.1. FTIR

Fourier transform infrared (FTIR) spectroscopy has proved to be a versatile tool to analyze cathode materials and could give information about the effect of intercalation molecules on the host structure. FTIR can be useful to confirm the presence of Ppy and PSA in the final hybrid material.

Fig. 4 shows the FTIR spectra of (3) PSA–Ppy/V_2O_5, (2) Ppy/V_2O_5 (both synthesised in $HClO_4$ acidic solution), (4) Ppy/V_2O_5 synthesised without $HClO_4$ acidic solution and (1) V_2O_5, in the frequency region 400–1800 cm^{-1}. The three strong

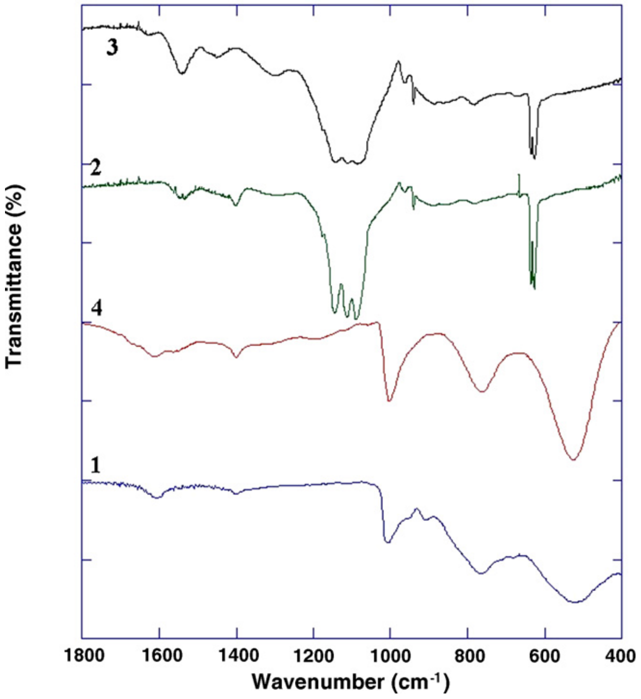

Fig. 4. FTIR spectra at room temperature of (3) PSA–Ppy/V_2O_5, (2) Ppy/V_2O_5 synthesised in acidic solution, (4) Ppy/V_2O_5 synthesised without acidic solution and (1) pristine V_2O_5.

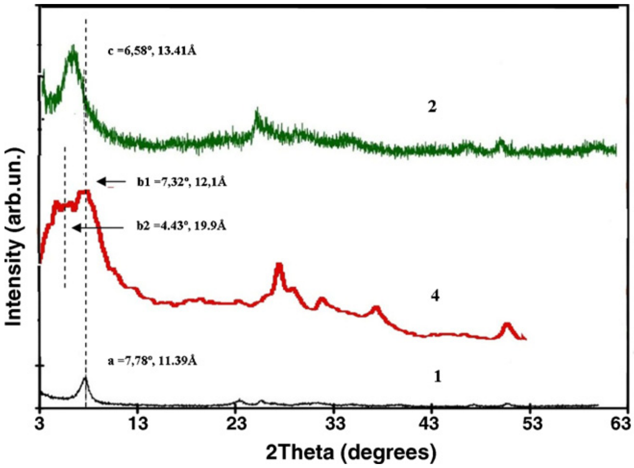

Fig. 5. X-ray diffraction patterns of as prepared: (1) V_2O_5, (4) Ppy/V_2O_5 synthesised without acidic solution and (2) Ppy/V_2O_5 synthesised in acidic solution.

bands below 1000 cm^{-1} on samples 1 and 4 are typical of vanadium–oxygen stretching. The bands at around 522 cm^{-1} and 760 cm^{-1} are due to symmetric and asymmetric V–O–V stretching. The vanadyl V=O vibration band is present around 1010 in the xerogel, which is likely to be sensitive to an out of plane chemical environment. In the case of the samples containing Ppy (Spectra: 2 and 3) these bands are less visible because of the absorbance of the Ppy and strong bands appearing at 1200 cm^{-1} and 600 cm^{-1}. The spectra of these materials show more bands in the 1000–1800 cm^{-1} region, corresponding to the typical Ppy pattern, and indicate the presence of Ppy in the sample (1530 cm^{-1}). Apart from the bands associated to the vanadium or Ppy compounds, in samples 3 and 2 two strong bands appear at 630 cm^{-1} and 1112 cm^{-1} in the hybrid material. These are related to the perchlorate from $HClO_4$ used to dissolve the V_2O_5 before the hybrid synthesis. However, there is no signal characteristic of the SO_3^- group of the additive which can be attributed either to the small concentration of the additive in the final hybrid material or because the signal is hidden by other bands, as they appear in the 1000–1200 cm^{-1} interval.

3.2. XRD

Powder XRD patterns of the V_2O_5 xerogel before and after intercalation of Ppy are given in Fig. 5. The XRD analysis confirms the intercalation of organic polymers into layers of V_2O_5 from the shift to lower angles of the (0 0 1) reflections upon intercalation. When acidic solution is used to disperse the vanadium oxide before the Ppy formation, interlayer expansion from (a) 11.39 Å to (c) 13.41 Å is observed. This interlayer expansion of about 2 Å is in accordance with previous reports for the organic polymer intercalation [7]. This suggests that parallel polymer chains lie between the V_2O_5 slabs. The exact structure of the hybrid material cannot be resolved from the powder XRD, and a random distribution of the polymer in the V_2O_5 interlayer is usually assumed.

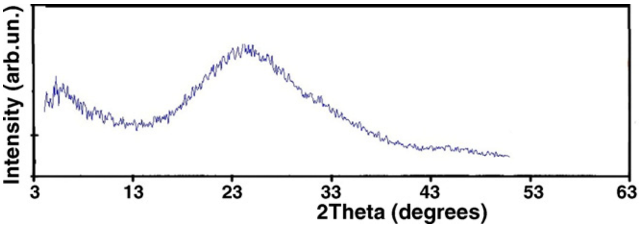

Fig. 6. X-ray diffraction patterns of as prepared PSA–Ppy/V_2O_5.

When the hybrid formation is carried out without acidic solution (4), two different maxima can be assigned to the lower angle-shifted (0 0 1) plane (b1 and b2). In b2, the polymer is intercalated between oxide layers, and in b1 no polymer is polymerised between oxide layers and the vanadium oxide maintains the primary structure. These results are based on the presence of the maximum at lower angles (b2) while the first one is located at similar values to the pristine V_2O_5 ones. This can be due to steric difficulties for the monomer molecules to penetrate inside the vanadium structure. As a consequence, the polymerization inside the inorganic host becomes more difficult. Hence, after the intercalation–polymerization process, a non-homogeneous vanadium oxide with Ppy is obtained in these conditions, as was suggested by the discharge profile.

In Fig. 6 the powder XRD of the PSA–Ppy/V_2O_5 is shown. In this case the material has greater amorphous nature, but the interlayer expansion is also more significant (17 Å) than in the hybrid synthesised without additive (13.41 Å). These kind of XRD patterns are similar to those shown in the literature for V_2O_5 aerogels [38] to explain the intercalation of polyaniline (PAni) in V_2O_5 [7,39]. It could be due to the higher polymerization degree of pyrrole monomers inside the inorganic host resulting in a greater percentage of polymer in the final hybrid material and greater separation between layers, due to the presence of PSA.

Table 1
Elemental analysis of the hybrid material synthesised in three different ways: (4) without acid solution or additive, (2) with acid solution and without additive and (3) with acid solution and additive

	(4) $Ppy_3V_2O_5$	(2) $Ppy_3V_2O_5 + HClO_4$	(3) $Ppy_3V_2O_5 + PSA + HClO_4$
Starting, *C* (%)	38.1	38.1	38.1
Final, *C* (%)	4.93	10.95	26.1
Final, *S* (%)	0	0	0.3
Experimental composition	$Ppy_{0.2}V_2O_5$	$Ppy_{0.53}V_2O_5$	$(PSA)_{0.06}Ppy_{1.63}V_2O_5$
Capacity (mAh g^{-1})	98	135	160

Table 2
Differences between the observed discharge capacity values (Table 1) and those expected for the sum of the individual capacities of Ppy and V_2O_5 contents considered separately

	Synthesis	V_2O_5 capacity	Ppy capacity	Sum of capacities	Experimental capacity	Difference (%)
Ppy (5)		0	90		90	
V_2O_5 (1)		120	0		120	
$Ppy_{0.2}V_2O_5$ (4)	Without acid	(111)	(6)	(117)	85	−32
$Ppy_{0.53}V_2O_5$ (2)	With acid	(100)	(15)	(115)	135	17
$(PSA)_{0.06}Ppy_{1.63}V_2O_5$ (3)	With acid and additive	(75)	(34)	(109)	160	50

Under parentheses expected theoretical capacity contribution from each component in each hybrid.

3.3. Elemental analysis

For all synthesised hybrids the elemental analysis (Table 1) shows that the ratio of Ppy:V_2O_5 is not maintained constant. Although the starting ratio in the solution was 3:1, the final ratio depends on the synthesis method. The percentage of carbon in the elemental analysis result gives the quantity of organic material that the sample contains, while the sulphur percentage could only be related to the PSA content in the hybrid material.

For sample 4, synthesised without acidic solution and additive, the final ratio is 0.2:1. A small amount of Ppy has been polymerised inside the inorganic matrix. This small amount of Ppy could be not enough to provide the needed conductivity for the electrode. Moreover, this Ppy is only intercalated in part of the V_2O_5 as observed by XRD. The consequence of this small conductivity was displayed in Fig. 2b, where the hybrid material shows less discharge capacity than the V_2O_5 xerogel with carbon black.

The small amount of Ppy synthesised inside the inorganic host could be attributed to two main reasons:

1. There is enough space for the pyrrole monomer to enter the inorganic matrix but not for the free movement of the monomers inside the inorganic matrix. Therefore the pyrrole cannot be efficiently oxidized by the vanadium atoms.
2. The vanadium oxidative strength in not sufficient to oxidize the monomer.

In sample 2, synthesised in an acidic solution without additive, the Ppy:V_2O_5 ratio increases to 0.5:1. The increase in the amount of organic material is mainly due to V_2O_5 particles in acidic solution exhibiting better oxidizing power [27,28]. Besides, the polymerization of pyrrole molecules can be affected by the acidic solution [40] and the acid-catalyzed condensation of pyrrole [41]. The presence of the acidic solution in the synthesis process will result in a hybrid with a higher amount of polymer.

When an acidic solution is used the xerogel structure dissolves and both, polymer and vanadium oxide precipitate together as oxidation of the monomer by the vanadium atoms occurs.

Finally, the Ppy:V_2O_5 ratio in the hybrid synthesised using additive is the highest (1.5:1), three times the one synthesised in acidic solution and eight times compared to the one without additive or acid.

3.4. Discharge capacity

The experimental compositions (Table 1) derived from the elemental analysis data also allow the detection of significant differences between the observed discharge capacity values (Fig. 2) and those expected from the sum of the individual capacities of the Ppy and V_2O_5 contents considered when separately, as shown in Table 2.

The hybrid synthesised without acidic solution shows less discharge capacity (−32%) than expected from the sum of individual capacities of its content of Ppy and V_2O_5. This supports the hypothesis of the non-homogeneous nature of this material. On the other hand, both hybrids synthesised in acidic solutions, addressed as homogeneous organic–inorganic hybrid in the discussion above, improve their capacities compared to the addition of each component. The hybrid synthesised with PSA improves its charge storage capacity to near 50% of the separate components. It proves that this kind of hybrid material takes advantage of the best properties of each component that form the hybrid, decreasing their drawbacks in an ideal synergic effect; which results in the development of the material with better properties.

4. Conclusions

Cointercalation of Ppy and PSA species into the V_2O_5 structure significantly changes the electrochemical behaviour of the hybrid material. The interaction of both organic species improves the capacity compared to both the V_2O_5 and the Ppy/V_2O_5 hybrid. This behaviour can be explained by two different reasons:

- The spacing between oxide layers is wider by the addition of the PSA. It would allow more space for the pyrrole monomers to enter the inorganic structure. If the pyrrole monomers arrive easier to the oxidizing points (vanadium atoms), the polymerization would be favoured and more polymer and more homogeneous hybrid would be formed, resulting in a hybrid material with better electrochemical properties.
- SO_3^- functional groups of the PSA organic compound would favour the chemical polymerization of polypyrrole inside the V_2O_5 structure.

Further investigations will be carried out in order to better understand the additive role and synthesize new and capacity-enhanced hybrid materials.

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References

[1] B.B. Owens, W.H. Smyrl, J.J.L. Xu, J. Power Sources 81–82 (1999) 150–155.
[2] J. Fan, P.S. Fedkiw, J. Power Sources 72 (1998) 165–173.
[3] T. Ohzuku, A. Ueda, Solid State Ionics 69 (1994) 201–211.
[4] J.M. Tarascon, D. Guyomard, Electrochim. Acta 38 (1993) 1221–1231.
[5] P. Novak, K. Mueller, K.S.V. Santhanam, O. Haas, Chem. Rev. 97 (1997) 207–281.
[6] P. Gomez Romero, Adv. Mater. 13 (2001) 163–174.
[7] G. Torres-Gómez, P. Gómez-Romero, Synth. Met. 98 (1998) 95–102.
[8] P. Gómez-Romero, G. Torres-Gómez, Adv. Mater. 12 (2000) 1454–1456.
[9] G. Torres-Gómez, E.M. Tejada-Rosales, P. Gómez-Romero, Chem. Mater. 13 (2001) 3693–3697.
[10] P. Gómez-Romero, N. Casañ-Pastor, M. Lira-Cantú, Solid State Ionics 101–103 (1997) 875–880.
[11] P. Gómez-Romero, M. Lira-Cantú, Adv. Mater. 9 (1997) 144–147.
[12] M. Lira-Cantú, P. Gómez-Romero, Chem. Mater. 10 (1998) 698–704.
[13] P. Gómez-Romero, M. Chojak, K. Cuentas-Gallegos, J.A. Asensio, P. Kulesza, N. Casañ-Pastor, M. Lira-Cantú, Electrochem. Commun. 5 (2003) 149–153.
[14] M. Lira-Cantú, P. Gómez-Romero, J. Electrochem. Soc. 146 (1999) 2029–2033.
[15] M. Lira-Cantú, P. Gómez-Romero, J. Solid State Chem. 147 (1999) 601–608.
[16] M.G. Kanatzidis, V. Petkov, P.N. Trikalitis, E.S. Bozin, S.J.L. Billinge, T. Vogt, J. Am. Chem. Soc. 124 (2002) 10157–10162.
[17] R. Enjalbert, J. Galy, Acta Crystallogr. C 42 (1986) 1467–1469.
[18] P. Aldebert, N. Baffier, N. Gharbi, J. Livage, Mater. Res. Bull. 16 (1981) 669–676.
[19] M.G. Kanatzidis, C.G. Wu, H. Marcy, J. Am. Chem. Soc. 111 (1989) 4139–4141.
[20] M.G. Kanatzidis, C.G. Wu, Ho Marcy, Chem. Mater. 2 (1990) 222–224.
[21] F. Huguenin, E.M. Gitotto, D.A. Buttry, J. Electroanal. Chem. 536 (2002) 37–45.
[22] S.G. Kang, K.M. Kim, S.H. Chang, J. Power Sources 133 (2004) 263–267.
[23] J. Harreld, H.P. Wong, L.F. Nazar, J. Non-Cryst. Solids 225 (1998) 319–324.
[24] G.R. Goward, F. Loroux, L.F. Nazar, Electrochim. Acta 43 (1998) 1307–1313.
[25] G.F. Demetz, F.J. Anaissi, H.E. Toma, Electrochim. Acta 46 (2000) 547–554.
[26] N.G. Park, K.S. Ryu, S.H. Chang, J. Power Sources 103 (2002) 273–279.
[27] S. Kuwabata, S. Masui, H. Tomiyori, H. Yoneyama, Electrochim. Acta 46 (2000) 91–97.
[28] S. Kuwabata, H. Tomiyori, J. Electrochem. Soc. 149 (2002) A988–A994.
[29] S. Kuwabata, S. Masui, H. Tomiyori, H. Yoneyama, Macromol. Symp. 156 (2000) 213–221.
[30] B. Ackermans, R.A. Schoonheydt, E. Ruizhitzky, J. Chem. Soc., Faraday Trans. 92 (1996) 4479–4484.
[31] M.L. Rojas-Cervantes, B. Casal, P. Aranda, et al., Colloid Polym. Sci. 279 (2001) 990–1004.
[32] E. Ruizhitzky, B. Casal, J. Chem. Soc., Faraday Trans. 1 85 (1989) 4167–4177.
[33] B. Casal, E. Ruizhitzky, M. Crespim, J.C. Galván, J. Chem. Soc., Faraday Trans. 1 (82) (1986) 1597–1605.
[34] K.T. Song, J.Y. Lee, H.D. Kim, D.Y. Kim, S.Y. Kim, C.Y. Kim, Synth. Met. 110 (2000) 57–63.
[35] J. Stejskal, M. Omastová, S. Fedorova, J. Prokes, M. Trchová, Polymer 44 (2003) 1353–1358.
[36] J. Joo, J.K. Lee, J.S. Baeck, K.H. Kim, E.J. Oh, J. Epstein, Synth. Met. 117 (2001) 45–51.
[37] J. Livage, Chem. Mater. 3 (1991) 578–593.
[38] H.P. Wong, B.C. Dave, F. Leroux, J. Harreld, B. Dunn, L.F. Nazar, J. Mater. Chem. 8 (4) (1998) 1019–1027.
[39] P. Gomez-Romero, C. Sanchez, Functional Hybrid Materials, Wiley, 2004.
[40] S.J. Hawkins, N.M. Ratcliffe, J. Mater. Chem. 10 (2002) 2057–2062.
[41] R.A. Jones, G.P. Bean, The Chemistry of Pyrroles, Academic Press, London, 1977.