

Short communication

## Influence of acids in the Ppy/V<sub>2</sub>O<sub>5</sub> hybrid synthesis and performance as a cathode material

I. Boyano<sup>a,\*</sup>, M. Bengoechea<sup>a</sup>, I. de Meatza<sup>a</sup>, O. Miguel<sup>a</sup>, I. Cantero<sup>b</sup>,  
E. Ochoteco<sup>a</sup>, H. Grande<sup>a</sup>, M. Lira-Cantú<sup>c</sup>, P. Gomez-Romero<sup>c</sup>

<sup>a</sup> CIDETEC, Energy Department, Paseo Miramón 196, Parque Tecnológico de San Sebastián, 20009 San Sebastián, Guipúzcoa, Spain

<sup>b</sup> CEGASA, C/Artapadura, 11, 01013 Vitoria-Gasteiz, Alava, Spain

<sup>c</sup> Instituto de Ciencia de Materiales de Barcelona (CSIC) Campus UAB, 08193 Bellaterra, Barcelona, Spain

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### Abstract

Vanadium oxide (V<sub>2</sub>O<sub>5</sub>) is a candidate as cathodic material for lithium ion batteries. With the aim of improving the electrode performance, Polypyrrole (Ppy) has been proposed as binder and conducting element in the oxide structure. The hybrid synthesis has been carried out in the literature by chemical polymerization of Pyrrole in the host inorganic matrix, in some cases using the V<sub>2</sub>O<sub>5</sub> dispersed in an acidic solution as an oxidizing agent. The hybrid material can be prepared using different acidic solutions that can influence the polymerization process affecting the electrochemical properties of the final hybrid material. The reasons and consequences for this influence are discussed and analyzed using different experimental techniques.

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**Keywords:** Lithium ion; Battery; Vanadium oxide; Xerogel; Hybrid material; Polypyrrole

### 1. Introduction

Cathodes formed from transition metal oxides demonstrate high specific capacity and energy density and good cyclability which are the characteristics more frequently searched for use in lithium ion batteries [1–3]. One way to improve the metal oxide cathodes is to use organic/inorganic hybrid materials in an attempt to obtain synergistic effects. In this context, vanadium pentoxide xerogels (V<sub>2</sub>O<sub>5</sub>) constitute ideal hosts for the intercalation of a large variety of species, between which conducting polymers stand out.

Kanatzidis et al. started fundamental work on the hybrid synthesis in 1989 [4,5]. The formation of hybrids of conducting polymers inserted in V<sub>2</sub>O<sub>5</sub> 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 stressing that while the inserted polymer is partially oxidized during the process, the V<sub>2</sub>O<sub>5</sub> itself suffers a partial reduction that renders it an electrically conductive mixed-

valence (V<sup>IV</sup>/V<sup>V</sup>) oxide [6]. The hybrid material has higher electronic conductivity and lower crystallinity than the pristine V<sub>2</sub>O<sub>5</sub> xerogel. These seem to be the reasons for the improvement of the charge–discharge behaviour. Many attempts have been made to use these V<sub>2</sub>O<sub>5</sub>/conducting polymer hybrid materials as a cathode in lithium-ion batteries, since then, several authors have reported such hybrids in a number of studies [7–12]. Kuwabata et al. have studied Ppy/V<sub>2</sub>O<sub>5</sub> hybrids formed by chemical polymerization of pyrrole using V<sub>2</sub>O<sub>5</sub> powder dispersed in an HClO<sub>4</sub> acidic solution as oxidizing agent [13–15]. Following this methodology, simultaneous polymerization and precipitation of the hybrid material occurred. Good results were obtained compared to those hybrids synthesized without acidic solution, especially in the enhancement of charge–discharge capacity.

Following Kuwabata's results, it would be interesting to test different acids in the synthesis in order to find the system with better electrochemical properties and understand the acid influence. Depending on the nature of the acid, it would affect (positively or negatively) the process by

- (1) Dissolving the xerogel structure: pyrrole monomers reach the VO<sub>2</sub><sup>+</sup> oxidation points (V<sup>5+</sup> oxoanion in solution) easier. Polymerization would be favoured and it will occur with

\* Corresponding author.

E-mail address: [iboyano@cidetec.es](mailto:iboyano@cidetec.es) (I. Boyano).

simultaneous precipitation of the formed hybrid. This hybrid could presumably contain a higher amount of intercalated polymer. If the xerogel is not dissolved, only the monomers in proximity to  $V^{5+}$  (either intercalated or on the particle surface) would polymerize. This supposition can be confirmed by the elemental analysis of the materials which can indicate the organic/inorganic ratio of the obtained material.

- (2) Reducing  $V^{5+}$  to  $V^{4+}$ : The reducing power of the acidic solution would decrease the amount of  $V^{5+}$  present, both in the solid (if the xerogel is not dissolved) and the liquid (as  $VO^{2+}$ ). Fewer oxidizing points would yield less quantity of polymer formed, with a negative effect on the final electrochemical properties of the hybrid material.
- (3) Inducing acid-catalyzed condensation of pyrrole [16,17]: if the polymerization is acid catalyzed the resulting polymer would have lower conductivity. Besides, this polymerization process would be independent to the vanadium present in the solution: the polymer would form outside the inorganic structure and mixture of organic and inorganic material would be obtained instead of a hybrid material. Electrochemical behaviour and structure of the final material can be affected by the catalytic function of the acid solution.

The objective of this article is to study the influence of different acid solutions and analyze which of them can improve the discharge capacity, the cyclability and different electrochemical properties of the hybrid cathode. Different types of acids have been tested: strong inorganic acids as  $HClO_4$  ( $pK_a = -7$ ) or  $H_2SO_4$  ( $pK_a = -3$ ), medium inorganic acids as  $HCl$  ( $pK_a = -1$ ) and weak organic acids as oxalic acid ( $C_2H_2O_4$ ;  $pK_a = 1.27$ ) or acetic acid ( $C_2H_4O_2$ ;  $pK_a = 4.76$ ).

## 2. Experimental methods

### 2.1. Materials and procedures

Experimental procedures used for hybrid material synthesis are described below.

#### 2.1.1. $V_2O_5$ xerogel

Synthesis of the  $V_2O_5 \cdot H_2O$  xerogel was carried out by the cationic exchange method. Briefly, 4.5 g of sodium metavanadate ( $NaVO_3$ ; Sigma) were dissolved in water at  $80^\circ C$ . Once cold, the solution was passed through a cationic exchange resin DOWEX 2x-100 (Sigma). The initial colourless solution changed to yellow-orange corresponding to the formation of the metavanadic acid. The concentration of  $V_2O_5 \cdot H_2O$  in the gel was analyzed by potentiometric titration method described elsewhere [18] with a CRISON pH meter and  $Ag/AgCl$  electrode: 2 ml of  $V_2O_5 \cdot H_2O$  xerogel 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  $H_2SO_4$  0.25 M; Carlo Erba). A final vanadium xerogel concentration of about 0.35 M is typically obtained.

#### 2.1.2. Ppy/ $V_2O_5$ hybrid synthesis

12.5 ml of the  $V_2O_5 \cdot H_2O$  xerogel were dispersed in 25 ml of ultrapure water. The solution was deaerated by bubbling  $N_2$

through it for 10 min. 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/ $V_2O_5$  hybrid. 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/ $V_2O_5$ hybrid synthesis in acidic solution

The hybrid synthesis in acidic solution was carried out in the same way as in the original synthesis, using 1 M solution of  $HClO_4$ ,  $H_2SO_4$ ,  $HCl$ , oxalic acid ( $C_2H_2O_4$ ) and acetic acid ( $C_2H_4O_2$ ) (all of them from Aldrich) instead of ultrapure water.

## 2.2. Characterization techniques

X-ray powder diffraction data were collected using a Philips X'Pert diffractometer (Bragg–Brentano geometry;  $CuK\alpha$ ; graphite secondary monochromator; range  $1.8^\circ$ – $50^\circ$   $2\theta$ ; step  $0.025^\circ$   $2\theta$ ; 2 s per step). Elemental analysis was carried out using a Perkin-Elmer 2400 CHN.

Electrochemical studies of the synthesized materials were performed in Swagelok type cells assembled in a glove box (LabMaster 130 MBraun). Lithium was used as negative electrode (anode) cut in 8 mm diameter discs. Five milligrams of Ppy/ $V_2O_5$  hybrid material were used as the positive electrode (cathode), by compressing the powder on an aluminium current collector at 40 bar for 5 min. A solution of 1 M  $LiPF_6$  in EC/DMC (50:50 in volume; Merck) is used as electrolyte. The measurements were performed on a Macpile-II potentiostat–galvanostat system under a constant current density in order to charge/discharge at  $C/40$  in the 4–2 V range.

## 3. Results and discussion

To distinguish the main effect of the acidic solution XRD, elemental analysis, electrochemical discharge and observation of solution changes during synthesis could be useful tools.

### 3.1. Synthesis behaviour

The mixture process of the vanadium xerogel with the acid solution before adding pyrrole is an important step that could provide information about the electrochemical quality of the final hybrid material. The analysis of the mixture properties will show if the vanadium oxide is completely dissolved or not (which would lead to different mechanisms for the polymerization) and the oxidation state of the vanadium atoms present in the solution.

The amount of  $V_2O_5 \cdot H_2O$  gel after being dissolved in the acidic solution was analyzed by a potentiometric titration method described in the experimental methods, where the  $V_2O_5 \cdot H_2O$  gel is analyzed with  $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ . The final concentration of  $V^{5+}$  obtained is related to the possibility of forming the hybrid, as the  $V^{5+}$  is needed in order to oxidize the monomer.

Table 1 summarizes some characteristics before adding the pyrrole monomer: colour, appearance and the  $V^{5+}$  content in

Table 1  
The colour and the state of the vanadium–acid system before adding the pyrrole monomer

Acid	Solution degree	Mixture colour	V <sup>5+</sup> acid/V <sup>5+</sup> ini	Final material (mg)
HCl	Dispersion	Green-brown	0	20
H <sub>2</sub> SO <sub>4</sub>	Dispersion	Green-brown	0	14.6
Oxalic acid (C <sub>2</sub> H <sub>2</sub> O <sub>4</sub> )	Dispersion	Dark orange	0	4.1
Acetic acid (C <sub>2</sub> H <sub>4</sub> O <sub>2</sub> )	Dispersion	Orange	0.3	37.3
HClO <sub>4</sub>	Dissolution	Light yellow	0.75	22.6

acid solution related to initial concentration (0.7 M). The mass of the finally obtained Ppy/V<sub>2</sub>O<sub>5</sub> is also shown.

The solution with higher concentration of V<sup>5+</sup> was obtained with HClO<sub>4</sub> which produces a transparent yellow solution from the original cloudy and dense V<sub>2</sub>O<sub>5</sub> xerogel solution. Thus the V<sub>2</sub>O<sub>5</sub> xerogel has been dissolved completely. Other acids dissolve the structure of the xerogel too, but as the solution is opaque, it can be deduced that this dissolution is not complete and part of the inorganic structure still remains not dissolved. Therefore, the insertion of the Py molecules into the layered structure is sterically hindered; the polymerization by the vanadium is less favoured and less material would be obtained.

These results contrast with the final mass of material shown in Table 1, where the mass of synthesized material is not correlated with the concentration of V<sup>5+</sup>: perchloric acid solution has more concentration of V<sup>5+</sup> but yields less material than acetic acid, and values of HCl and H<sub>2</sub>SO<sub>4</sub> are close to HClO<sub>4</sub> (samples of similar weight to the ones of HClO<sub>4</sub>). These results can be explained by the acid-catalyzed condensation of pyrrole. The presence of the acidic solution in the synthesis will catalyze the polymerization reaction resulting in a material with a higher amount of polymer. By the acid-catalyzed polymerization a polymer with less conductivity is obtained, and the polymerization takes place outside the inorganic matrix. The result of this polymerization will be a non-structured material with a high proportion of non-active polymer, with small charge storage capacity (Fig. 1).

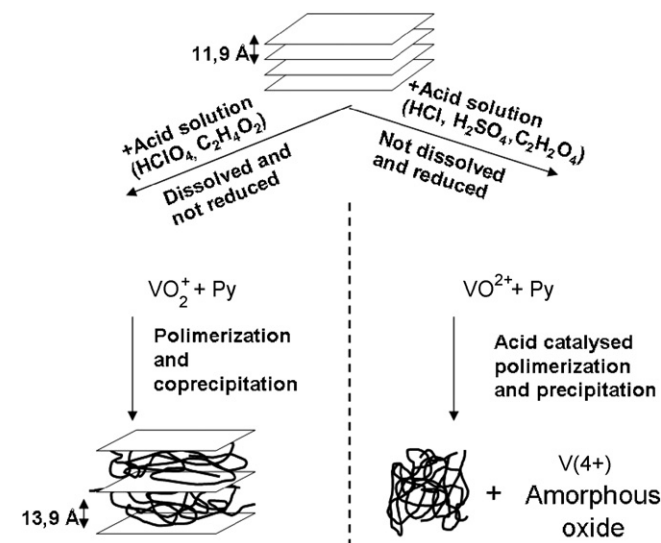


Fig. 1. Scheme of differences in the final material synthesized by the oxidation polymerization by V<sup>5+</sup> or by the acid catalysed polymerization in absence of V<sup>5+</sup>.

The acid catalyzed polymerization will compete with the polymerization carried out by V<sup>5+</sup> molecules and validity of the material for being used as electrode in lithium ion batteries is related to this competition. Better electrochemical properties will be achieved by a material with higher quantity of intercalated polymer (not necessary the same as the polymer ratio in the material).

Vanadium has multiple oxidation states from +5 to +2 and varies with the pH of the solution. In this case, as the reaction is carried out under acidic conditions, the main ion present is VO<sup>2+</sup>, known as the dioxovanadium (V) ion. A useful clue to find out the oxidation state, is related to the colour of the vanadium depending on the valence, as the V<sup>5+</sup> solutions are yellow in colour, V<sup>4+</sup> blue and the mixed valence solution, green. The colour of the vanadium–acid solution could be representative of the oxidation state of the vanadium atoms. The higher the oxidation state, the higher the oxidation power towards Py, resulting in a material with better properties for using it as a cathode in a lithium ion battery. A high concentration of V<sup>5+</sup> will compete with the acid-catalyzed polymerization probably giving higher conducting polymers.

An important result shown in Table 1 is related to the quantity of V<sup>5+</sup> in the acid–xerogel solution. In the HCl, H<sub>2</sub>SO<sub>4</sub> and oxalic acid (C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>) water solutions, it is not possible to quantify the V<sup>5+</sup> concentrations by means of potentiometric titration, therefore it can be deduced that the concentration is zero. The V<sup>5+</sup> concentration gives an idea of the oxidation power of the vanadium xerogel solution. The less V<sup>5+</sup> ions present, the less pyrrole polymerization in the vanadium oxide structure and the less hybrid material would be obtained.

Nevertheless, it must be determined whether the material obtained is a hybrid material synthesized by the oxidation on the vanadium atoms, or two phase material due to the influence of the acidic condensation. The elemental analysis (proportion of organic/inorganic material) and X-ray diffraction (the structure of the material) can help to discriminate between them.

### 3.2. XRD

XRD analysis could confirm the intercalation of organic polymer into layers of V<sub>2</sub>O<sub>5</sub> from the shift to lower angles of the (001) reflection upon intercalation. The powder XRD pattern of the V<sub>2</sub>O<sub>5</sub> xerogel is given in Fig. 2 together with those of the hybrid materials synthesized in HCl, H<sub>2</sub>SO<sub>4</sub>, HClO<sub>4</sub>, oxalic acid (C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>) and acetic acid (C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>) solution. When HClO<sub>4</sub> and acetic acid solution is used, interlayer expansion from 11.39

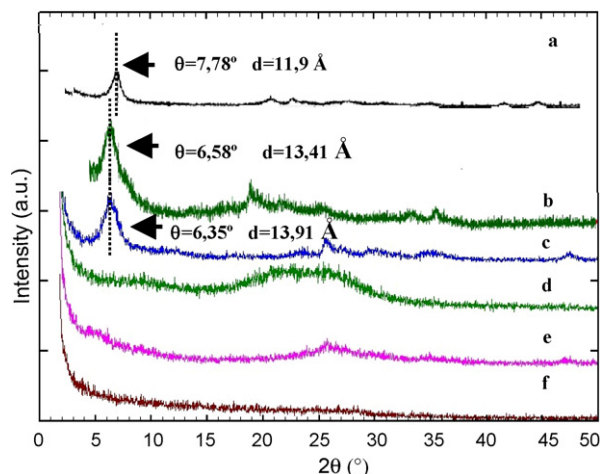


Fig. 2. X-ray diffraction patterns of (a)  $V_2O_5$  xerogel and Ppy/ $V_2O_5$  hybrid material synthesized in acidic solution of (b)  $HClO_4$ , (c) acetic acid ( $C_2H_4O_2$ ), (d)  $HCl$ , (e)  $H_2SO_4$  and (f) oxalic acid ( $C_2H_2O_4$ ).

to 13.91 and 13.41 Å is observed. This interlayer expansion of about 2 Å is in accordance with previous reports for the organic polymer intercalation [19]. This suggests that a parallel polymer chain lies between the  $V_2O_5$  slabs. The structure of the hybrid material cannot be solved from the powder XRD, and a random distribution of the polymer in the  $V_2O_5$  interlayer is usually assumed.

When the hybrid formation is carried out with other acidic solutions such as  $HCl$ ,  $H_2SO_4$  and oxalic acid, no maximum is observed and can be assumed that either the oxide laminar structure is destroyed and/or the main part of the polymer is polymerized outside the inorganic structure giving the material an amorphous nature. This absence of structure will have a negative result in the final discharge of the hybrid, as will be seen later in the electrochemical behaviour of different samples. As shown in Fig. 2, the hybrid material synthesized with acetic acid maintains the laminar structure resulting in a better discharge capacity. In this medium, vanadium atoms will be in solution and the polymerization occurs because atoms of vanadium polymerize pyrrole molecules inside the laminar structure.

### 3.3. Elemental analysis

Table 2 shows the starting and final ratio of monomer and vanadium, the theoretical formula of the final material and the

Table 2

Elemental analysis of the hybrid material synthesized without acid and using different acidic solutions:  $HClO_4$ ,  $HCl$ ,  $H_2SO_4$ , oxalic acid ( $C_2H_2O_4$ ) and acetic acid ( $C_2H_4O_2$ )

Starting composition	Final N %	Final C %	Experimental composition	Capacity ( $mAh\ g^{-1}$ )
$Py_3V_2O_5$	1.2	4.93	$Ppy_{0.2}V_2O_5$	98
$Py_3V_2O_5 + HClO_4$	2.6	10.95	$Ppy_{0.53}V_2O_5$	135
$Py_3V_2O_5 + HCl$	7.6	29.4	$Ppy_2V_2O_5$	18
$Py_3V_2O_5 + C_2H_4O_2$	1.7	7.52	$Ppy_{0.33}V_2O_5$	60
$Py_3V_2O_5 + H_2SO_4$	8.5	35.1	$Ppy_{2.8}V_2O_5$	7
$Py_3V_2O_5 + C_2H_2O_4$	6.5	25.8	$Ppy_{1.6}V_2O_5$	20

Py, pyrrole monomer; Ppy, polymerized monomer.

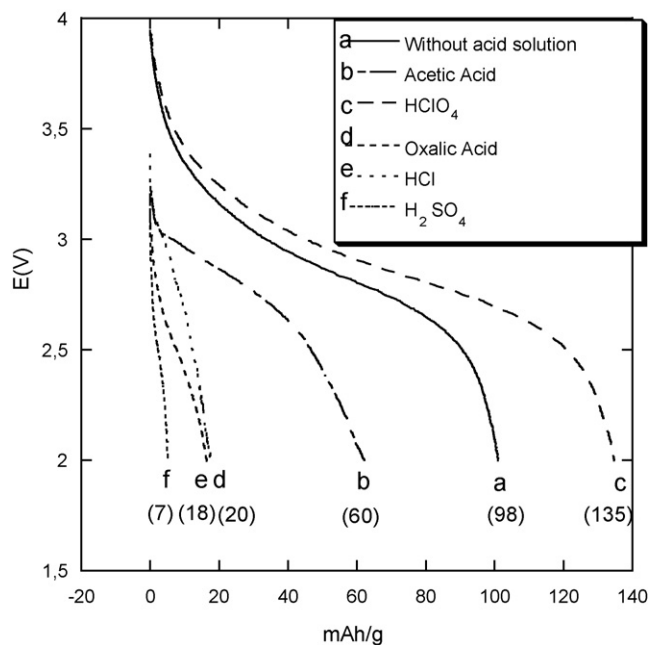


Fig. 3. Discharge curves for (a) the Ppy/ $V_2O_5$  hybrid synthesized without acidic solution and in acidic solution of (b) acetic acid ( $C_2H_4O_2$ ), (c)  $HClO_4$ , (d) oxalic acid ( $C_2H_2O_4$ ), (e)  $HCl$  and (f)  $H_2SO_4$ . Data were collected at  $C/40$  discharge rate in 4–2 V range. Under brackets values of discharge capacities in  $mAh\ g^{-1}$  are shown.

discharge capacity of each sample. As expected, in all the samples analyzed, the percentage of carbon varies from sample to sample. These values are related to the quantity of polymer that forms the final material.

Results show that the nature of the acid greatly influences the amount of Ppy being polymerized. The amount of Ppy polymerized in  $HCl$ ,  $H_2SO_4$ , oxalic acid and acetic acid is not enough to provide the necessary conductivity for the electrode, since the properties of the final material are not only related to the amount of polymer but also to the conductivity of said polymer and the location where it has been polymerized (outside or inside the slabs). The consequence of this small conductivity is displayed in Fig. 3, where the hybrid material shows less discharge capacity than the  $V_2O_5$  xerogel.

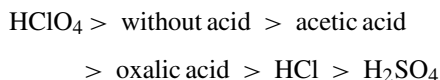
In the sample with  $HClO_4$ , the Ppy: $V_2O_5$  ratio is 0.5:1. The quantity and quality of the polymer in this case seems to be ideal to get good results as the hybrid material improves the discharge capacity of vanadium electrode.

### 3.4. Electrochemical behaviour

#### 3.4.1. First cycle discharge

Differences on the first cycle discharge capacity are shown in Fig. 3. In this figure the discharge curves for the Ppy/V<sub>2</sub>O<sub>5</sub> hybrid synthesized without acidic solution and in acidic solution of HCl, H<sub>2</sub>SO<sub>4</sub>, HClO<sub>4</sub>, oxalic acid and acetic acid are compared. This figure is used to analyse the influence of the acidic solution in the final hybrid material used as cathode in a lithium ion battery.

If arranged from the best capacity to the lowest:



As can be seen, only the influence of HClO<sub>4</sub> is beneficial to the capacity.

Their starting discharge potential can be separated in two groups:

- Oxalic acid, HCl, acetic acid and H<sub>2</sub>SO<sub>4</sub>. The starting discharge potential is around 3.5 V. It can be related to the reaction between the acid and Vanadium (V), which results in a partial reduction of the vanadium and in a worse polymerization. This behaviour is supported by results in Table 1 where the colour change in the solution indicates the redox reaction.
- HClO<sub>4</sub> and hybrid without acid. The starting discharge potential is around 4 V. This result, together with the colour of

the solution shown in Table 1, indicates that the HClO<sub>4</sub> solution dissolves the V<sub>2</sub>O<sub>5</sub> xerogel structure without reducing V<sup>5+</sup> to V<sup>4+</sup>.

#### 3.4.2. Cyclability

In Fig. 4 the cyclability of the hybrid synthesized with HCl, H<sub>2</sub>SO<sub>4</sub>, HClO<sub>4</sub>, oxalic acid, acetic acid, and another hybrid synthesized without acid, can be observed. As shown in Fig. 4, the use of perchloric acid improves not only the specific capacity of the hybrid material but the cyclability as well. After 30 cycles, the capacity of the hybrid material is around 120 mAh g<sup>-1</sup>, while the hybrid synthesized without acid drops from 98 to 75 mAh g<sup>-1</sup>. The influence of the other acids, as has been explained, is damaging to the charge storage properties, although the discharge capacity remains constant.

## 4. Conclusions

The effect of the acid solution on the intercalation of Ppy into the V<sub>2</sub>O<sub>5</sub> structure significantly changes the electrochemical behaviour of the hybrid material. The influence of different acids has been tested: HCl, H<sub>2</sub>SO<sub>4</sub>, HClO<sub>4</sub>, oxalic acid and acetic acid.

Only the HClO<sub>4</sub> improves the discharge capacity and the cyclability of the hybrid cathode. The improvement of the capacity was obtained when the acid solution dissolves the inorganic structure, without reducing the vanadium atoms, and then coprecipitates the organic and inorganic material obtaining the intercalated hybrid material.

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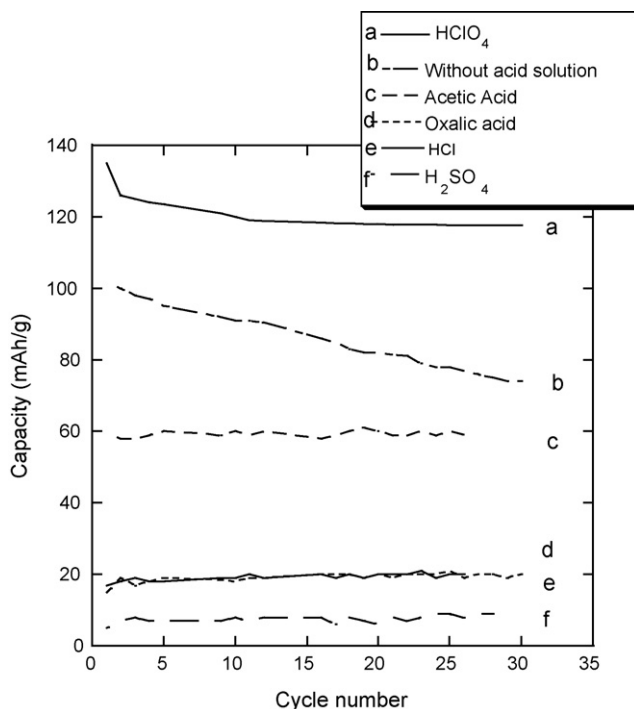


Fig. 4. Cyclability of (b) the Ppy/V<sub>2</sub>O<sub>5</sub> hybrid synthesized without acidic solution and in acidic solution of (a) HClO<sub>4</sub>, (c) acetic acid, (d) oxalic acid, (e) HCl, (f) H<sub>2</sub>SO<sub>4</sub>. Data were collected at C/40 discharge rate in 4–2 V range.

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