



Preparation of C-LiFePO₄/polypyrrole lithium rechargeable cathode by consecutive potential steps electrodeposition

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ABSTRACT

In this work carbon coated lithium iron phosphate (C-LiFePO₄)/polypyrrole (PPy) composite preparation has been carried out using electrochemical techniques. This composite has been deposited on a stainless steel mesh in order to use it as a cathode in a lithium-ion battery. When an oxidation potential is applied to the working electrode, the pyrrole monomer is polymerized and the C-LiFePO₄ particles are incorporated into the polymer matrix and bound to the polymer and mesh. An experimental procedure was performed in order to understand how the composite formation is carried out and what the oxidation state of the composite material is during the charge–discharge process. As the electrochemical method of synthesis has a big influence in the electrochemical properties of the polymer, the use of consecutive potential steps has been studied in order to improve the charge–storage capacity of the composite material. The influence on the final composite properties of the oxidation–deposition time and potential and the effect of the number of cycles has been analyzed. An improvement of about 20% has been achieved using short oxidation times (3 s) at 0.9 V vs. Ag/AgCl. The reasons for this improvement are discussed and analyzed using different experimental techniques.

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1. Introduction

Lithium-ion (Li-ion) batteries are key components of many portable electronic devices and are emerging in the hybrid and full electric vehicle market as well as many other applications. Electrode materials should possess both high Li conductivity and electronic conductivity to facilitate the easy insertion of Li ions and charge transfer. Due to their low electronic conductivities, bad adhesion to the current collector and deficient cohesion between particles, the electrode active materials (LiCoO₂, LiMn₂O₄ and LiFePO₄) are required to blend with electro-conductive additives and binders when used as cathode materials [1–3].

Binder materials are electrochemically stable and indispensable for the electrode properties [4] such as the permanent adhesion of the active materials to the aluminum and copper collector, which is decisive for the long-life properties of a battery. The PVDF family products are most adopted as a binder in the traditional lithium-ion battery industry. On the other hand, electro-conductive additives effectively enhance the charge–discharge rate and the cycle-life of the Li-ion batteries. For this purpose, conductive carbon parti-

cles, such as acetylene black, Ketjen black, carbon nanotubes, and graphite, are usually employed [5–7].

The use of these electrochemically inactive materials has the drawback of reducing the energy and power densities of the corresponding electrodes [2]. Achieving homogeneous dispersions of carbon and PVDF particles in matrix materials is usually a difficult task, and this is especially true when dispersion in a highly dense suspension is required [6]. If the particles are heterogeneously dispersed, performance, yield and safety of the resulting battery are greatly lowered [8].

Optimization on the electrode components is important for the development of Li-ion batteries with high performance and long cycle-life. One way to improve the energy storage capacity of the metal oxide cathodic electrodes is to use intrinsically conducting polymers as an electrode component, with the advantage of an improved performance without the addition of any other binding or conducting agent. Composites of conjugated polymers such as polypyrrole or polyaniline, are interesting because of their potential for combining electronic conductivity and binding properties.

Composites based on conducting polymer and transition metal oxides (LiCoO₂, LiMn₂O₄, V₂O₅ and LiFePO₄) have been investigated during recent years due to their potential applications as electrode material in lithium batteries. Much of this work has been made

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using chemically synthesized PPy [9–12] or with another conducting polymer such as PEDOT [13–15].

Recently, Goodenough et al. [16–18] have shown that replacement of the inactive carbon black and PTFE materials by polypyrrole (PPy) enhances the capacity and rate capability of the composite cathode based on carbon coated lithium iron phosphate (C-LiFePO₄). The composite C-LiFePO₄/PPy cathodes are prepared in situ by deposition on stainless steel mesh by cyclic voltammetry technique. During the PPy polymerization onto the mesh, C-LiFePO₄ particles are incorporated into the polymer matrix and bound to the polymer. The use of PPy as conducting polymer is very interesting because its charge–discharge process occurs reversibly from –0.9 to 0.4 V vs. Ag/AgCl, that is, about 2.4–3.7 V vs. Li/Li⁺, thus contributing to the C-LiFePO₄ reaction (3.45 V vs. Li/Li⁺).

The electrochemical polymerization process is more accurate and gives the chance to have a better control of synthesis parameters and reactions than the chemical route [19]. The electrochemical oxidation of monomers, pyrrole for example, initiates a polymerization process at the electrode/electrolyte interface that promotes the formation of a polymeric film that adheres to the electrode. Electrochemically initiated polymerization of conducting polymers comprises fast and complex reactions giving a mix of polymer chains with different properties [20]. Any physical, chemical or electrochemical property of the attained material is a function of the obtained composition. The composition of every film is influenced by the way that experimental conditions of synthesis act on the relative rates of the simultaneous reactions occurring during current flow. Then, it is possible to design experimental conditions of synthesis to produce materials with improved charge-storage capacity and electric conductivity for battery applications.

In this work, the influence of different preparation conditions was studied using consecutive potential steps in the polymerization-deposition method. The polymerization by consecutive potential steps allows a better control of the electrochemical parameters. For example, compared to cyclic voltammetry electrodeposition, better control of the exact time and potential of the oxidation process can be achieved. The electrodeposition conditions of the C-LiFePO₄/PPy composite material have been studied in order to obtain an electrode with improved charge-storage capacity.

2. Experimental methods

C-LiFePO₄/PPy composite cathodes were prepared by in situ electrodeposition. The starting C-LiFePO₄ was provided by Phostech Lithium, Inc., Montréal, Canada. The carbon coating on the C-LiFePO₄ particles improves their performance in lithium-ion rechargeable batteries and in this case, also allows anchoring of the PPy [17]. A certain amount of pyrrole (Py) monomer was mixed with 25 mg of C-LiFePO₄ fine powder in 10 mL acetonitrile containing 0.1 mol L⁻¹ LiClO₄ as an electrolyte. The concentration of Py was changed to obtain composites with different polymer weight fraction in the composite; the suspension was sonicated for 10 min and stirred during electrodeposition. The working electrode for the deposition was a 100-mesh stainless steel. The counter electrode was 100-mesh stainless steel, and Ag/AgCl was used as reference electrode. Composite deposition was performed by cyclic voltammetry and consecutive potential steps (square waves) techniques on a Biologic MPG system. Voltammetric experiments were performed over 20 cycles from 0 to 1.3 V at a scanning rate of 100 mV s⁻¹. The consecutive potential steps were performed at different oxidation potentials (from 0.9 to 1.3 V) and different oxidation times (3, 5 and 7 s), to 3 s of reduction time at –0.1 V. Both techniques were performed in a nitrogen atmosphere.

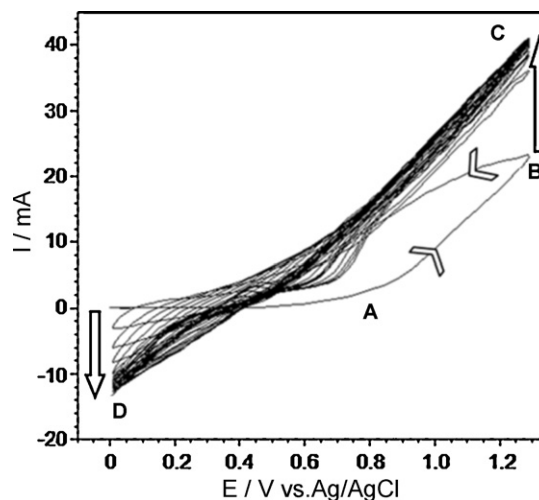


Fig. 1. Cyclic voltammetric curve for the electrodeposition of the C-LiFePO₄/PPy cathode.

Electrochemical characterization of the electrodes was carried out in Swagelok cells. The C-LiFePO₄/PPy films deposited on the stainless steel mesh were used directly as the cathode without addition of either Carbon black or PVDF. Metallic lithium foil was used as counter and reference electrode; the electrolyte was 1 mol L⁻¹ LiPF₆ in a 1:1 solvent mixture of ethylene carbonate and dimethyl carbonate (EC/DMC). The cells were assembled in a glove box; the electrochemical tests were controlled with an MPG system and performed between 2 and 4 V vs. Li⁺/Li at C/10 and room temperature. The electrochemical characteristics of the C-LiFePO₄/PPy composites were compared to cathodes prepared from a mixture of C-LiFePO₄, C-black, and PVDF (80:11:9, wt%) with an area of 0.5 cm² and a total mass of 5–7 mg on aluminum substrate. These electrodes were prepared by two different ways: from a slurry deposited in the aluminum substrate, and physically mixed in a mortar and pressed to form a pellet over the aluminum substrate. The specific capacity values obtained are referred in all cases to milliamp per gram of electrode and not only to gram of C-LiFePO₄.

The PPy content in the C-LiFePO₄/PPy composites was analyzed by thermogravimetric analysis (TGA, Perkin-Elmer) in Argon atmosphere. The micrographies of the composite electrodes were taken at an accelerating voltage of 30 kV by a scanning electron microscope (JEOL JSM5500LM). Powder diffraction patterns of oxidized and reduced composites were collected in a Bruker D8 Advance diffractometer working with Cu K α radiation at room temperature.

3. Results and discussion

3.1. Analysis of composite deposition in cyclic voltammetry conditions

In order to understand how the deposition process takes place, deposition on stainless steel mesh with cyclic voltammetry was performed during 20 cycles at 100 mV s⁻¹ sweep rate from 0 to 1.3 V vs. Ag/AgCl. As an electrolyte, 10 mL acetonitrile containing 0.1 mol L⁻¹ LiClO₄ was used in which 0.4 mol L⁻¹ of pyrrole (Py) monomer and 25 mg of C-LiFePO₄ powder were dissolved. A composite electrode loading of 6 mg cm⁻² was obtained with 20 wt% of PPy. These experimental conditions of composite preparation were described by Goodenough et al. in a previous work [16]. Fig. 1 shows the 20 voltammetry cycles for the deposition of this composite cathode.

The voltammogram of the composite deposition shown in Fig. 1 is comparable to the pyrrole electrodeposition performed at similar

experimental conditions [21]. The pyrrole oxidation occurs above 0.8 V vs. Ag/AgCl (point A in Fig. 1), and the oxidized monomer is deposited as black powder on the stainless steel mesh.

The polymerization–deposition by cyclic voltammetry process takes place in a continuous way and only the first cycle differs from the others, where a nucleation and growth process can be observed (as shown in Fig. 1 point B by the direction of the arrows in the intensity curve). During the monomer oxidation and deposition, the C-LiFePO₄ particles are incorporated into the polymer matrix and bound to the polymer [16]. As C-LiFePO₄ is oxidized above 3.45 V vs. Li⁺/Li (0.15 V vs. Ag/AgCl), the composite and monomer oxidation can be carried out in this potential window as the pyrrole is oxidized from 0.8 to 1.3 V vs. Ag/AgCl.

Different experiments were carried out in order to understand the composite formation and the oxidation state of the C-LiFePO₄ in the composite. Fig. 2 shows cyclic voltammetry curves in a wider potential window (–0.5 and 1.5 V Ag/AgCl) chosen in order to analyze the electrochemical response of the materials at the potentials used later in this study.

The results of three different experiments are shown in Fig. 2: firstly, the stainless steel mesh has been cycled alone in 1 M LiClO₄ acetonitrile solution (Fig. 2a), in order to analyze the influence of the mesh on the experimental data of the composite. Secondly (Fig. 2b), the electrolyte solution is stirred and mixed with C-LiFePO₄ in order to ascertain if the iron phosphate may be oxidized and deposited without pyrrole. Finally, 10 mg of C-LiFePO₄ powder has been pressed to the stainless steel mesh without any binder or conducting material and cycled in the 1 M LiClO₄ acetonitrile solution (Fig. 2c). The pressed C-LiFePO₄ powder has been cycled in the electrolyte without pyrrole monomer with the aim of observing its influence in the overall composite oxidation and reduction signal.

As expected, the stainless steel mesh does not interfere in the composite oxidation and reduction. The low intensity shown in Fig. 2a confirms the electrochemical stability of the mesh in that potential window.

When C-LiFePO₄ powder is dispersed in the electrolyte (Fig. 2b), no more additional electrochemical activity is observed; therefore C-LiFePO₄ particles alone cannot be oxidized over a stainless steel electrode. Moreover, the mesh appears without any deposition when the cyclic voltammetry is finished. This fact confirms that the C-LiFePO₄ powder cannot be deposited without a conducting polymer monomer in that potential window. However, when C-LiFePO₄ is previously pressed to the stainless steel electrode, the C-LiFePO₄ is reversibly oxidized to FePO₄ in the –0.5 to 1.5 V Ag/AgCl potential window. The high intensity shown in Fig. 2c corroborates this assumption.

Apart from the experiments shown in Fig. 2, the composite C-LiFePO₄/PPy was analyzed by X-ray diffraction at oxidized and reduced state. The electrooxidized sample was cycled in the 0–1.3 V Ag/AgCl potential window and stopped when the composite is oxidized (Fig. 1, point C), whereas the electroreduced sample was stopped when the cyclic voltammogram is at 0 V vs. Ag/AgCl (Fig. 1, point D). In Fig. 3, X-ray diffraction measurements of composites at 1.3 V (electrooxidation) and 0 V (on subsequent electroreduction) are shown.

The X-ray diffraction data of the composite at 0 V vs. Ag/AgCl (Fig. 3, pattern D) show peaks corresponding to the triphylite C-LiFePO₄ phase (JCPDS, PDF-2 no. 01-70-6684) while the material formed on electrooxidation (pattern C) is indexed as the oxidized heterosite, FePO₄ (JCPDS no. 01-70-6685). As expected by the cyclic voltammetry experiments, these results indicate that during oxidation potential, the monomers are polymerized and oxidized together with C-LiFePO₄, giving as a result a mix of oxidized polymer and FePO₄ particles. At reduction potentials (0 V vs. Ag/AgCl), the inorganic and polymeric components of the composite are reversibly reduced.

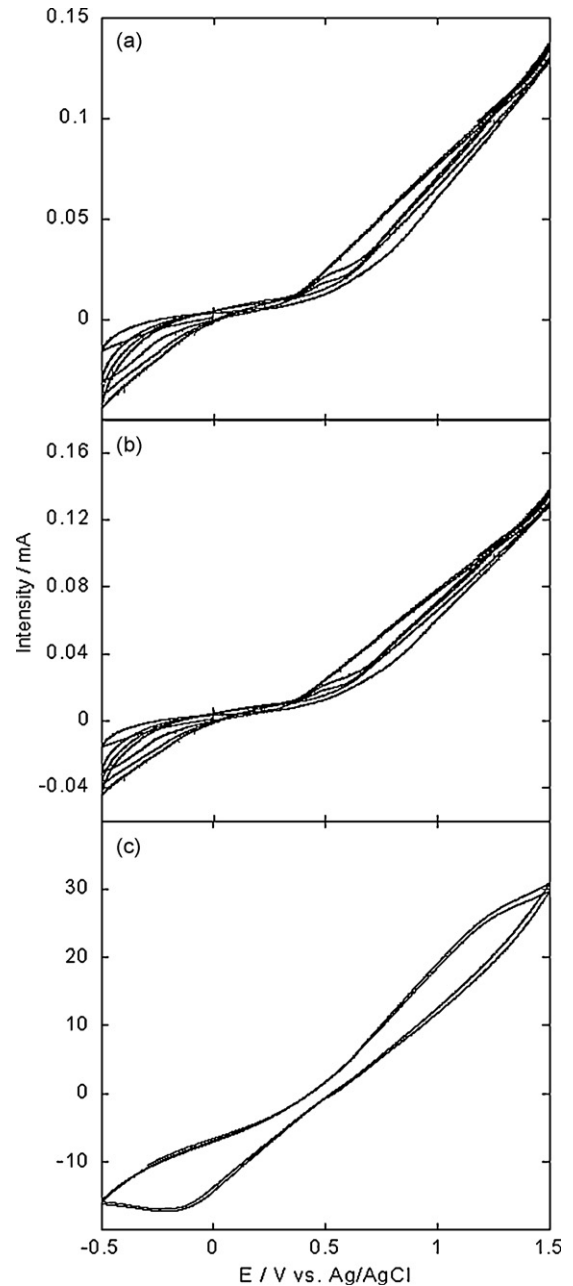
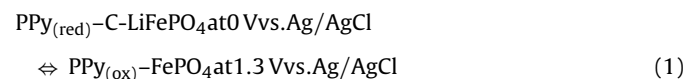
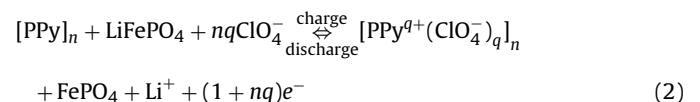


Fig. 2. Cyclic voltammeteries performed in the –0.5 to 1.5 V vs. Ag/AgCl potential window at 100 mV s^{–1} to (a) stainless steel mesh in 1 M LiClO₄ acetonitrile solution, (b) the same experiment adding C-LiFePO₄ to the solution and (c) 10 mg of C-LiFePO₄ powder pressed to the stainless steel mesh in 1 M LiClO₄ acetonitrile solution without pyrrole.

Eq. (1) shows the schematic composite structure and oxidation state as a function of the potential:



Therefore, the mechanism of oxidation/reduction of the C-LiFePO₄/PPy composite in the range from 0 to 1.3 V vs. Ag/AgCl is as follows:



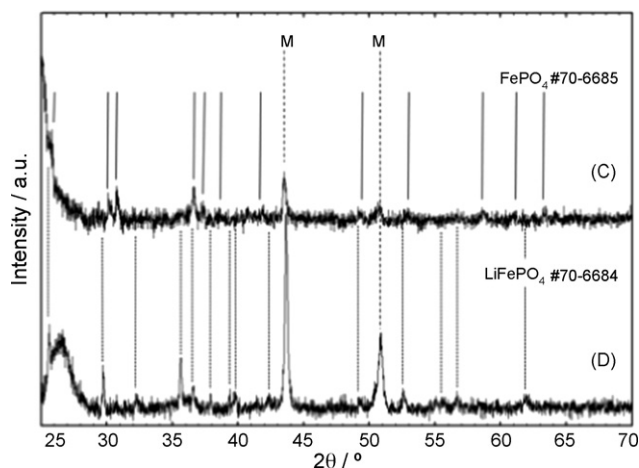


Fig. 3. XRD patterns of the C-LiFePO₄/PPy composite at the oxidized potential (C) and after reduction (D). Lines labeled as M refer to the stainless steel mesh where the composite is deposited.

Table 1

Fixed and studied parameters in the composite deposition by consecutive potential steps.

| | |
|-------------------------------------|---|
| Fixed parameters | |
| Reduction time | 3 s |
| C-LiFePO ₄ concentration | 0.02 M |
| Pyrrole concentration | 0.4 M |
| Electrolyte solution | 0.1 M LiClO ₄ in acetonitrile |
| Electrode distance | 0.8 cm |
| Solution stirring | |
| Studied parameters | |
| Oxidation potential | 0.9, 1.0, 1.1, 1.2 and 1.3 V vs. Ag/AgCl |
| Oxidation time | 3, 5 and 7 s |
| Number of steps | 15, 30, 45 and 60 |
| Reduction potential | -0.1, -0.2, -0.3, -0.4 and -0.5 V vs. Ag/AgCl |

where n is the degree of polymerization and q is the doping level of the polymer.

3.2. Composite deposition by consecutive potential steps

The aim of this work is to improve the reference characteristics of the C-LiFePO₄/PPy electrodeposited composite by modifying the electrochemical technique, using consecutive potential steps in the polymerization-deposition process. The polymerization by consecutive potential steps allows a better control of the electrochemical parameters and, for example, the exact time and potential of the oxidation process can be defined.

With a better definition of the polymerization parameters, the nucleation and growth of the polymer can be controlled. Managing the growth and morphology of the polymer could have a big influence on the percentage of polymer in the composite and its conductivity. In Table 1 are shown the values of the consecutive potential steps parameters. Some of them are fixed and others have been varied in order to study its influence.

The polymerization by consecutive potential steps involves periods of oxidation-polymerization, followed by reduction steps. One of the advantages of introducing these reduction steps is the elimination by convection of the concentration gradient of pyrrole and C-LiFePO₄ at the electrode electrolyte interface. It has been considered 3 s as enough time to eliminate the concentration gradient.

Moreover, during this period of time, the conducting polymer is reduced, extracting anions and compacting the polymeric structure [22,23]. This compression would promote a better trapping of the C-LiFePO₄ in the polymer matrix. This process would increase the amount of inorganic material on the electrode.

Fig. 4 shows the chronoamperometric signals for composite electrodeposition process performed by 60 consecutive potential steps when 7 s of oxidation time is applied. Fig. 4a shows the first six oxidation/reduction steps of the chronoamperogram shown in Fig. 4b.

The first anodic step of the chronoamperometric polymerization (Fig. 4a) promotes the monomer oxidation and polymer nucleation on stainless steel mesh. In subsequent anodic steps, polymer and inorganic material oxidation plus a monomer oxidation-phosphate deposition take place, both on the electrode surface. A greater charge is necessary to reduce the FePO₄ and the polymer present on the electrode during cathodic steps; this observation indicates that the thickness of the composite layer is increasing at each new step. Every change of the applied voltage results in an instantaneous maximum or minimum in the chronoamperometric response that may be associated to a resistance change or a double-layer charge. In previous studies of deposition of conducting polymers by potential step technique, this phenomenon is assigned to the charge of the electrical double layer at the polymer-solution interface [23].

In order to identify the intensity associated to two processes (composite oxidation and C-LiFePO₄/PPy composite electrodeposition), the schematic Fig. 4c has been plotted. As the oxidation/reduction reaction of the composite is reversible, the corresponding charges are symmetrical. Then graphically, the polymerization charge can be distinguished as the difference between the overall oxidation charge and the charge used to oxidize the composite.

The consecutive cathodic steps will provide the flow of electric charge necessary to reduce and compress the polymer chains together with the FePO₄ reduction to C-LiFePO₄. As can be observed in Fig. 4c, at the starting stages of deposition, the oxidation charge is bigger than the reduction charge. The reason for this difference is related to the complex oxidation that takes place in the stainless steel electrode; it is formed by two processes: the polymerization of the monomer and the oxidation of the composite.

At the starting stages of oxidation, when the amount of deposited composite over the electrode is low, the polymerization-deposition process is the dominant one. As the mass of deposited composite increases, the composite oxidation becomes the important process in comparison to the polymerization reaction. Then, lower charge is used to polymerize the monomer molecules as the number of steps increases.

As explained above, the use of polymerization steps instead of cyclic voltammetry makes it possible to have a better control of the polymerization time and potential. If the deposition process is carried out by cyclic voltammetry, the oxidation potential changes continuously and it is difficult to control its evolution with time. Managing the exact time and oxidation potential allows a perfect control of the polymerization process.

As the polymerization-deposition process is stopped at reduction potential, the composite obtained is in C-LiFePO₄-PPy_(red) form. In all cases, a good, uniform mixing between the C-LiFePO₄ and PPy can be observed from the images of the scanning electron micrograph (SEM) of Fig. 5. A good adherence of the composite to the mesh is obtained.

Once the composite is prepared, the properties of the final material must be measured in order to analyze whether it is suitable to be used as an electrode in lithium-ion batteries. First of all, the electrode composition (percentage of conducting polymer) and deposited mass (mg cm⁻²) are chosen as reference characteristics in order to understand the relationship between the synthesis conditions and final composition of the electrode. Once the deposition characteristics are known, the relationship between the composition and specific capacity values (mAh g⁻¹) will be analyzed.

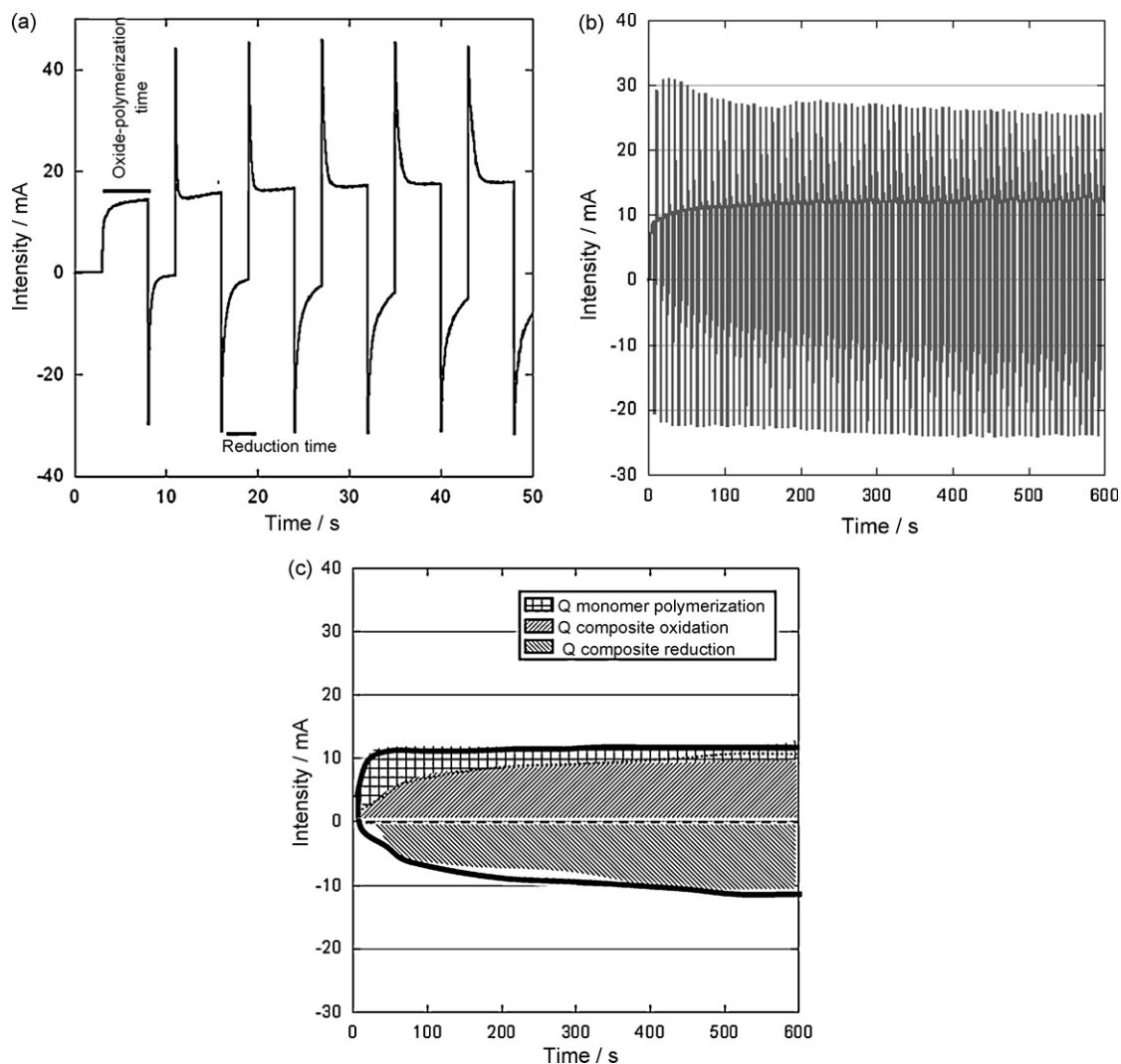


Fig. 4. Potential step behavior for the electrodeposition process of the C-LiFePO₄/PPy cathode: (a) shows the first six oxidation/reduction steps of the chronoamperogram shown in (b). A schematic sight of the charge evolution of the composite deposition process is represented in (c).

3.3. Synthesis conditions vs. final composition of the electrode

In Fig. 6 the electrode mass in milligrams per square centimeter and percentage of PPy in the composite are related to the synthesis conditions of each composite. These data correspond to the potential steps performed from -0.1 V during 3 s to 0.9 V vs. Ag/AgCl. Different reduction potentials were previously analyzed (-0.1 , -0.2 , -0.3 , -0.4 and -0.5 V vs. Ag/AgCl), but no significant differences were observed in the deposited samples. Only variations below 5% in the mass of C-LiFePO₄ were achieved between samples polymerized at different reduction potentials.

The relative rates of nucleation and growth processes of conducting polymers on stainless steel electrodes can be a function of the pulse characteristics. The results presented in Fig. 6 clearly show that the C-LiFePO₄/PPy composite deposition behavior therefore depends on the duration of each oxidation pulse and the number of pulses that influence the polymerization-deposition process of the polymer. For this reason, the mass and percentage of polymer of composites deposited at similar overall deposition time (oxidation step time multiplied by the number of steps) are different.

The parameter that seems to control the composite formation is the oxidation step time. Fig. 6 shows linear dependence of electrode mass and percentage of polymer on oxidation step time.

As explained before, when the first anodic (oxidation) step is applied, the oxidation of pyrrole molecules and the deposition of PPy on the stainless steel mesh take place. During this process the carbon coating of the C-LiFePO₄ particles promotes the bonding of the C-LiFePO₄ to the PPy [17]. During the reduction step, the composite is reduced, compacting the structure and eliminating the concentration gradient of pyrrole and C-LiFePO₄ at the electrode interface. Then, when the second anodic step takes place, the deposited composite is oxidized and other pyrrole molecules are oxidized over the stainless steel mesh or over the previously deposited polymer adding new C-LiFePO₄ particles. This process could produce an increase of the polymer chain length (degree of polymerization) or the deposition of new short chains of polypyrrole over the previously deposited polymer. In any case, an increase of the deposited composite mass will be observed.

However, Fig. 6 shows that the lower the oxidation time, the higher is the electrode mass and smaller the percentage of polymer; and it has no correlation with the number of steps. Important differences in the percentage of polymer are clearly observed depending on the oxidation time varying from 19 to 32%. This effect can be explained by better trapping or better adhesion of the C-LiFePO₄ in the polymer matrix at short step times.

In the composite preparation, apart from the nucleation and growth that are the typical processes of conducting polymer

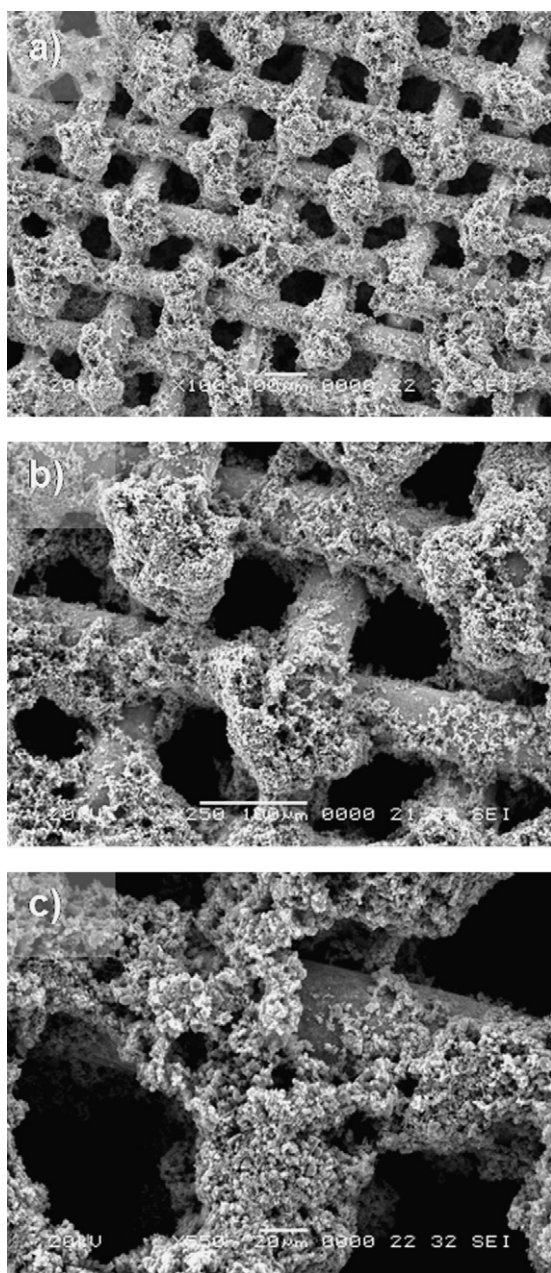


Fig. 5. SEM images for a C-LiFePO₄/PPy composite on steel mesh, amplified: (a) 50, (b) 250 and (c) 500 times.

electrodeposition, another process is also taking place: the precipitation of C-LiFePO₄ trapped in the polymer.

The decreasing weight of composite with increase of the oxidation time might be related to the bad adhesion of the formed composite to the electrode. At the oxidation potential, the monomers are polymerized and the inorganic material is trapped by the polymer, but the bad adhesion of the composite to the electrode promotes the precipitation of part of the composite and a weight loss during composite polymerization-deposition. Therefore, in the case of short oxidation step times (3 s), as the reduction step times are more frequent, less material is lost during electrochemical deposition.

The differences in PPy percentage relative to the oxidation step time can be associated to the C-LiFePO₄ concentration at the interface when the reduction step compacts the polymeric structure. When the composite is reduced, the inorganic material at the inter-

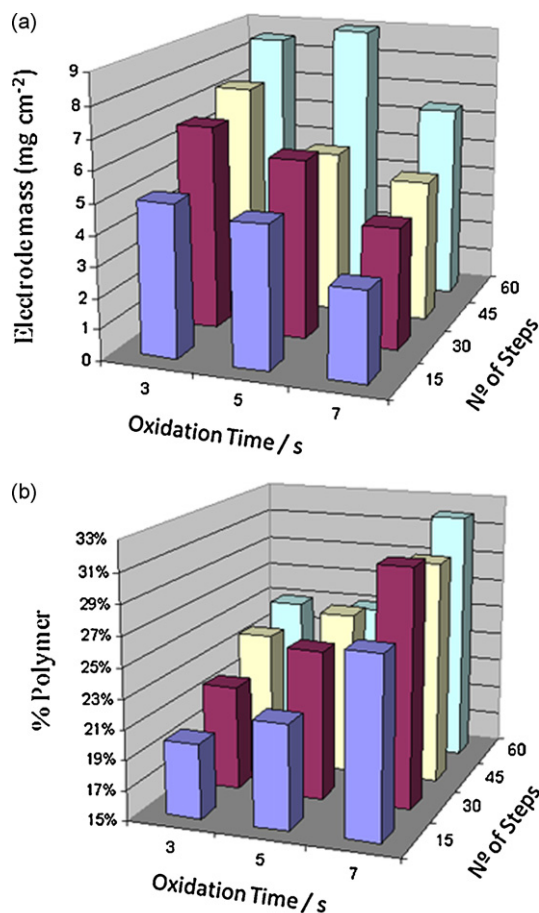


Fig. 6. Graphical view of composition (% of polymer) and deposited mass (mg cm⁻²) of composites, related to the polymerization conditions (number of steps and oxidation time of each step).

face is trapped by the polymer chains, and a higher C-LiFePO₄ concentration at the interface when the polymer is compacted results in a higher percentage of inorganic material attached to polymer chains.

Therefore, it can be concluded that at short step times the concentration of C-LiFePO₄ is higher at the polymer/oxide interface, promoted by the elimination of the concentration gradient by the reduction steps.

In any case, a big difference between composites is obtained depending on the anodic step conditions, which proves the influence of experimental conditions of synthesis on the final material composition. Therefore, by monitoring the synthesis process, composite properties can be controlled and specific materials matched to the application can be obtained.

3.4. Composition vs. composite capacity

The specific capacity values (mAh g⁻¹) of each composite as a function of the oxidation time and number of steps are shown in Fig. 7.

The experimental data of Fig. 7 clearly show that the shorter the oxidation time and number of steps, the better specific capacity values are obtained. It seems to be logical, since both parameters increase the amount of polymer in the composite (Fig. 6) and the charge-storage capacity of the polymeric material (90 mAh g⁻¹) [24] is lower than the theoretical value for C-LiFePO₄ (170 mAh g⁻¹). Oxidation times below 3 s were also studied, but the obtained weight of composite material after 60 cycles

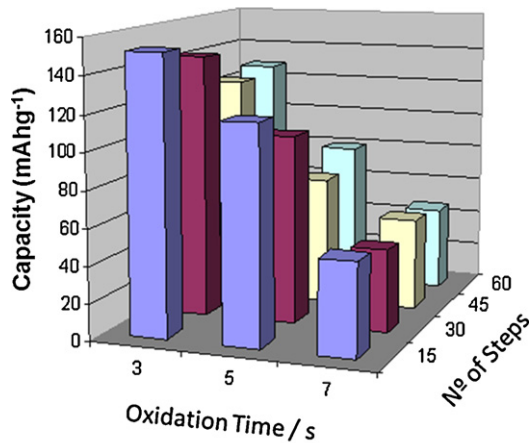


Fig. 7. Graphical view of specific capacity (mAh g^{-1}) of composites, related to the polymerization conditions.

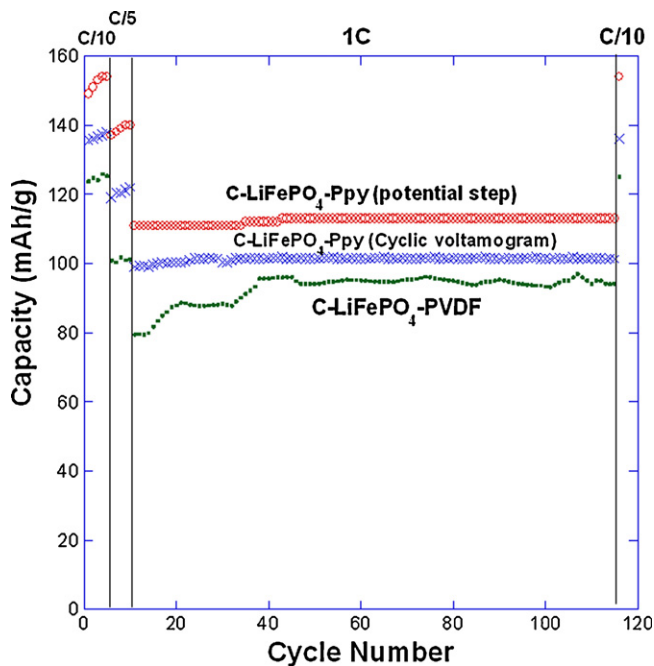


Fig. 8. Graphical view of specific capacity (mAh g^{-1}) of composite (C-LiFePO₄/PPy) synthesized at 3 s of oxidation time and 15 steps, related to the discharge rate. An electrode of C-LiFePO₄ + binder + conductive material (80:9:11, wt%), and a composite (C-LiFePO₄/PPy) electrodeposited by cyclic voltammogram are also presented for comparative purposes.

was not big enough to be practical as electrode of a lithium-ion battery.

The higher value for the specific capacity obtained experimentally is 154 mAh g^{-1} . This composite synthesized at 3 s of oxidation time and 15 steps, contains 20% of PPy. The experimental capacity matches well with the expected theoretical storage charge for the sum of each component:

$$\text{Exp. Cap. composite} = \text{Theoretical capacity LiFePO}_4 \times \%wt + \text{Theoretical capacity of PPy} \times \%wt$$

$$154 \text{ mAh g}^{-1} = 170 \text{ mAh g}^{-1} \times 80\% + 90 \text{ mAh g}^{-1} \times 20\% = 136 \text{ mAh g}^{-1} + 18 \text{ mAh g}^{-1}$$

It can be concluded that the 20% of PPy in the electrode is enough to act as binder and conducting material of the C-LiFePO₄ and, in addition, contributes to the improvement of the charge-storage capacity.

Moreover, the composite cathodes show a good cyclability. Fig. 8 illustrates specific capacity vs. cycle number, charged and

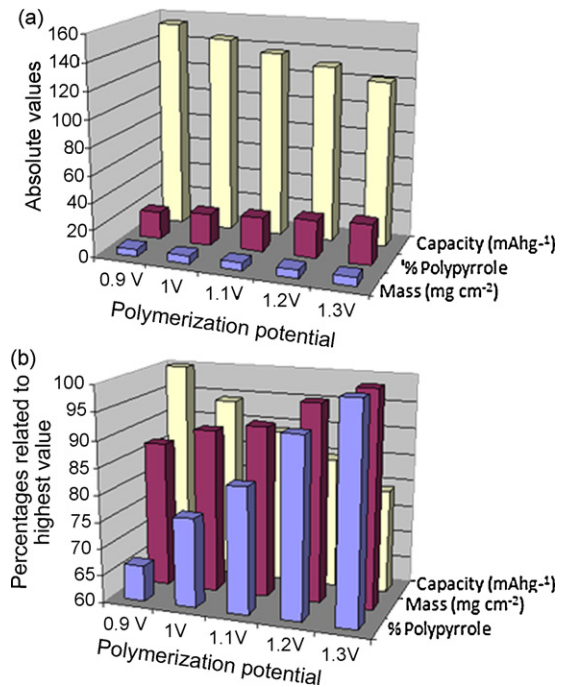


Fig. 9. Graphical view of the electrode composition (% of polymer), deposited mass (mg cm^{-2}) and specific capacity (mAh g^{-1}) of composites, related to the polymerization potential: (a) shows the absolute values and (b) represents the percentage related to the biggest value (6.2 mg cm^{-2} , 30% of PPy and 154 mAh g^{-1}).

discharged at different rates for a total of 120 cycles for the electrochemically synthesized C-LiFePO₄/PPy composite cathode (the composite was synthesized at the above-explained experimental conditions). This cyclability is compared to a composite (C-LiFePO₄/PPy) electrodeposited by cyclic voltammogram and C-LiFePO₄/PVDF/acetylene black electrode (80:9:11, wt%) discharged at 1C.

As can be observed, there is no fade in discharge capacity after 100 cycles at 1C. Finally, a last cycle at C/10 is made in order to see whether the specific capacity has been recovered and no degradation has occurred at the electrode. This result demonstrates that the structure of the composite is very stable and the electrochemical Li⁺-ion insertion/extraction process is quite reversible even at high rates.

4. Influence of polymerization potential

The previous data are related to the polymerizations made by oxidation steps at 0.9 V vs. Ag/AgCl. In order to analyze the influence of the oxidation potential in the final composite, a potential window from 0.9 to 1.3 V vs. Ag/AgCl has been chosen. Below this potential no polymerization reaction takes place, and above 1.3 V the PPy is not conductive enough to enhance the electrode properties.

According to the experimental results shown before, the best charge-storage capacity is obtained by 15 oxidation steps of oxidation during 3 s. Therefore, these polymerization conditions were

chosen and only the oxidation potential was changed to analyze its influence.

In Fig. 9, electrode composition (% of polymer), deposited mass (mg cm^{-2}) and specific capacity values (mAh g^{-1}) of composites prepared at different oxidation potentials are shown. In Fig. 9a, the data are presented in absolute values for each variable; and

Table 2
Differences in percentage between the experimental discharge capacity values of the electrode and those expected for the sum of the individual capacities of PPy and C-LiFePO₄ contents considered separately. Under brackets, expected theoretical capacity contribution from each component in each composite.

| | Prepared at | C-LiFePO ₄ capacity/mAh g ⁻¹ | PPy capacity/mAh g ⁻¹ | Sum of capacities | Experimentally capacity/mAh g ⁻¹ | Difference |
|----------------------------|-------------|--|----------------------------------|-------------------|---|------------|
| PPy | | 0 | 90 | | 90 | |
| C-LiFePO ₄ | | 170 × 0.8 = (136) | 0 | | 136 | |
| C-LiFePO ₄ /PPy | 0.9 V | 170 × 0.8 = (136) | 90 × 0.20 = (18) | (154) | 154 | 0% |
| C-LiFePO ₄ /PPy | 1.0 V | 170 × 0.77 = (131) | 90 × 0.23 = (21) | (152) | 145 | -4.7% |
| C-LiFePO ₄ /PPy | 1.1 V | 170 × 0.75 = (128) | 90 × 0.25 = (22) | (150) | 137 | -8.7% |
| C-LiFePO ₄ /PPy | 1.2 V | 170 × 0.72 = (122) | 90 × 0.28 = (25) | (147) | 130 | -11.6% |
| C-LiFePO ₄ /PPy | 1.3 V | 170 × 0.70 = (119) | 90 × 0.3 = (27) | (146) | 122 | -16.4% |

in Fig. 9b, the same values are presented in percentages related to the highest value of each series.

As expected, the final material composition and properties vary depending on the polymerization conditions. Results show that the oxidation potential influences the amount of PPy in the sample, the composite weight, and the specific charge-storage capacity. As the oxidation potential increases, the polymerization reaction is favored, which results in an increase of the percentage of polymer (from 20 to 30%) and the mass of the electrode (from 5.4 to 6.2 mg).

On the other hand, as the polymerization potential increases, the charge-storage capacity decreases (from 154 to 122 mAh g⁻¹). Two main factors have a big influence in this behavior: firstly, as explained above, the charge-storage capacity of the polymer is lower than the C-LiFePO₄, and then an increase in the polymer ratio above a threshold (20%) has no benefits in the charge-storage capacity of the composites. Secondly, as the polymerization potential increases, the electroactivity of the polymer is damaged because of reticulation and degradation reactions that take place during polymerization at such potentials [19]. The PPy deposited at 1.0, 1.1, 1.2 and 1.3 V vs. Ag/AgCl is not electroactive enough to provide the necessary conductivity for the electrode. The consequence of this lower electroactivity (and then, conductivity) is displayed in Fig. 9, where the composites polymerized at higher potential steps than 0.9 V vs. Ag/AgCl show less discharge capacity.

The quantity and conductivity of the polymer in the composite material seems to be ideal when it is polymerized at 0.9 V vs. Ag/AgCl, improving the capacity of C-LiFePO₄. The experimental compositions derived from the elemental analysis data also allow the detection of significant differences between the observed discharge capacity values and those expected from the sum of the individual capacities of the PPy and C-LiFePO₄ contents considered separately, as is shown in Table 2.

As shown in Table 2, the composite prepared at 0.9 V shows the same discharge capacity expected from the sum of both components. The composites prepared at 1.0, 1.1, 1.2 and 1.3 V vs. Ag/AgCl show less discharge capacity than expected from the sum of individual capacities of the content of PPy and C-LiFePO₄. This difference is higher as the oxidation potential increases. This observation supports the fact that the electroactivity of the polymeric material decreases depending on the polymerization potential. The material polymerized at 0.9 V plays the main role of binder and conducting material and, in addition, it contributes to the improvement of the charge-storage capacity.

It can be concluded that as the polymerization potential increases, the specific capacity of the composite decreases for two reasons: firstly, because the percentage of polymer increases and it has lower specific capacity (90 mAh g⁻¹ of PPy and 170 mAh g⁻¹ of C-LiFePO₄). Secondly, because at these polymerization potentials, the polymer is less electroactive and does not work properly as binder and conducting material, as is shown in Table 2.

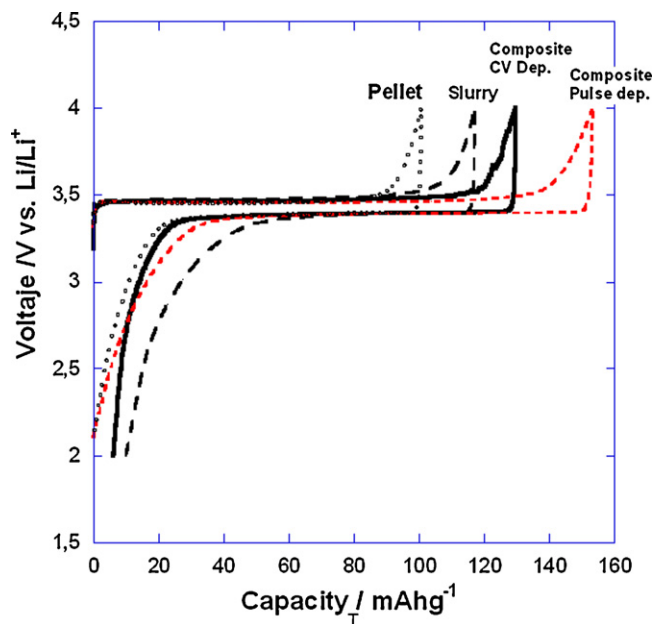


Fig. 10. Voltage vs. electrode capacity for a cathode formed by a pellet (···) and slurry (---) of C-LiFePO₄ + binder + conductive material (80:9:11, wt%), a composite material C-LiFePO₄/PPy electrodeposited by cyclic voltammogram (—) and C-LiFePO₄/PPy composite material by pulse deposition (— · —) (80:20, wt%) at a rate of C/10.

5. Composite cathode vs. conventional cathode

The aim of this work has been an electrode material with high specific capacity. The best results have been obtained with composites prepared by 15 potential steps of 3 s of oxidation at 0.9 V vs. Ag/AgCl and 3 s of reduction at -0.1 V. The obtained composite's charge-storage capacity is compared to two conventional cathodes, one of them prepared from a slurry deposited on an aluminum substrate as previously described, and the other, physically mixed in a mortar and pressed to form a pellet over the aluminum substrate (C-LiFePO₄ with carbon black and PVDF binder). In all cases the quantity of active material was the same (80%). The best specific capacity values are referred to milliamp per gram of electrode and not to gram of C-LiFePO₄. As can be seen in Fig. 10, an improvement of 20% has been obtained in the composite specific capacity related to the conventional cathodes. The enhancement of the specific capacity of the composite can be assigned to the contribution of the polymeric material to the charge-storage capacity.

In addition, the charge-storage capacity has been improved in comparison to the previously prepared composites by cyclic voltammetry at 1.3 V vs. Ag/AgCl (135 mAh g⁻¹) [17]. These results show the influence of the polymerization-deposition potential on the final electrode properties.

6. Conclusions

Composites of C-LiFePO₄/PPy with controlled properties have been obtained by consecutive potential steps as the electrodeposition method. As previously shown by cyclic voltammetry electrodeposition, the addition of the conducting polymer instead of electrochemically inactive carbons and binders keeps the composite film electrically conductive and with good adhesion to the current collector, important factors to develop Li-ion battery cathodes with high performance and long cycle-life.

The experimental results indicate that during electrodeposition, C-LiFePO₄ is oxidized to FePO₄ together with the oxidation-polymerization of the monomers. At reduction potentials, the inorganic and polymeric materials are reversibly reduced.

The influence of the polymerization-deposition parameters on the composite characteristics, such as the charge-storage capacity or material composition, has been analyzed. The use of consecutive potential steps as a preparation method allows a better control of the electrodeposition parameters. Composites prepared by 15 potential steps of 3 sconds of oxidation at 0.9V vs. Ag/AgCl are formed with 20% of polymeric material. This composition exhibits a maximum specific capacity of 154 mAh g⁻¹. This value is 20% higher than the conventional electrode with the same active material composition and gives also a 15% improvement on the composite obtained by cyclic voltammetry.

In this work, the electrodeposition conditions in order to obtain an electrode with improved electrochemical charge-storage capacity have been defined. The wide number of controlled parameters that can be changed in the consecutive potential step deposition would allow obtaining composites with tailored characteristics, for example the further improvement in the charge-discharge rate.

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