

Chemical reduction method for industrial application of undoped polypyrrole electrodes in lithium-ion batteries

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Abstract

This work describes a new method of chemical reduction of p-doped polypyrrole (Ppy) to make a graphite/Ppy lithium-ion battery. Several reducing agents are analysed (sodium hydrosulfite ($\text{Na}_2\text{S}_2\text{O}_4$), sodium hydrogensulfite ($\text{Na}_2\text{S}_2\text{O}_5$), hydroxymethanesulfonic acid monosodium salt ($\text{HOCH}_2\text{SOONa}$), sodium borohydride (NaBH_4), formamidinesulfonic acid ($\text{H}_2\text{NCNHSO}_2\text{H}$), stannous chloride (SnCl_2) and hydrazine (N_2H_4)), obtaining the best results when reducing a Ppy electrode with sodium borohydride (NaBH_4): at least 85% of the polymer electrode can be reduced without significant degradation. To verify the feasibility of the reduction method two lithium-ion batteries with a Ppy cathode have been assembled using different ways (4.5 cm \times 1.9 cm electrodes having similar active electrode material (mg cm^{-2}) values and thicknesses to commercial inorganic oxide electrodes). In one of them the doped Ppy electrode is previously electrochemically reduced, applying consecutive potentials steps before the cell assembling; it would be accurate and easy at laboratory scale, but from an industrial point of view it is complicated and not viable. In the second battery the doped Ppy electrode is chemically reduced resulting in a similar charge–discharge characteristic to the electrochemically reduced one. Therefore, the chemical reduction method can be a step forward for using Ppy as cathode in lithium-ion batteries at industry level. © 2006 Elsevier B.V. All rights reserved.

Keywords: Polypyrrole; Reductant; Chemical reduction; Lithium-ion; Battery

1. Introduction

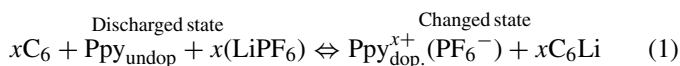
Great efforts have been made in order to find lithium-ion batteries which can solve the problems that nowadays persist in this energy storage device: higher energies, lower cost materials, more flexibility and safety. The solution can be partially found in inorganic materials such as olivine or nasicon type phosphates or manganese spinels, but they are not the unique possibility proposed. During the 1980s, certain industrial interest arose about conducting polymers, and their range of applications including electrodes and membranes for electrochemical energy conversion and storage devices, sensors [1,2], organic diodes [3,4] or artificial muscles [5–7]. Apart from the advantages inherent to their polymeric nature (i.e. chemical stability and compatibility, ease of manufacturing and low cost), they are also highly

conductive. Besides, as it can be repeatedly cycled between different oxidation states, this kind of polymers can be used as a reversible electrode for rechargeable batteries. Therefore, many polymers have been investigated and developed due to their potential industrial applicability in electrodes for rechargeable batteries [8–14] (as lithium [15–20] or lithium-ion batteries [21–24]). The advantages of using a polymer electrode as cathode are potentially higher specific capacities and lighter and more flexible cells, resulting from the light weight of the polymers. In this way a conducting polymer cathode (polyaniline electrode) was exploited by Japan's Bridgestone Company in the large-scale production of a high-cycle-life, button type 3 V battery [25].

In 1995, Beck and co-workers [22] developed the first lithium-ion battery with a p-doped polypyrrole (Ppy) cathode. They opened a way to build a new kind of rechargeable batteries with an electrochemically synthesized conducting polymer cathode. A Ppy electrode was electrochemically polymerized and afterwards, a second potentiostatic step was applied in a

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monomer-free electrolyte. Scrosati and co-workers [23,24] tried different prototypes showing good cyclability and an appreciable theoretical energy density (300 Wh kg^{-1} versus graphite). The polymer was also electrochemically generated and electrodes were preactivated by cycling versus a lithium electrode before combining them into the cell structure. They called them “dion” batteries since dual intercalation of both the lithium cations and the counteranions were involved in the electrochemical process. For example, by charging the cell using LiPF_6 salt, Li^+ cations are intercalated into the graphite structure while the PF_6^- are simultaneously injected into the Ppy structure. The opposite process occurs during the discharge (Eq. (1)).



In the previous examples the Ppy is obtained in oxidized state. So, the fresh graphite anode would be in discharged state and the Ppy cathode in charged state. The resulting cell would be useless and no redox reaction would occur. Then a previous Ppy undoping step before cell assembling is certainly needed. At laboratory scale the electrochemical reduction process is easier and more accurate but from an industrial point of view the chemical reduction [26–28] is simpler, cheaper and therefore, more viable. Although a large number of studies have been done using electrochemically reduced conducting polymer electrodes [21–24], small attention has been paid to the chemical reduction of these polymers synthesized by chemical oxidative polymerization.

The goal of this paper is to find a chemical method to reduce a doped Ppy electrode without degradation. It would increase the chances of developing a feasible industrial manufacturing process for graphite/Ppy lithium-ion batteries. In order to check the viability of this new reducing method, two lithium-ion batteries with Ppy electrodes will be prepared by reducing the doped Ppy electrode either chemically or electrochemically, and the results of both cells compared.

2. Experimental

2.1. Preparation of polypyrrole

2.1.1. Electrochemical Ppy

Polymer films were electropolymerized and checked in a one-compartment electrochemical cell, connected to a Voltalab 21 potentiostat–galvanostat and controlled via PC. Working electrode and counter electrode were platinum sheets with a 1 and 4 cm^2 surface area, respectively. A saturated calomel electrode (SCE) from Crison Instruments was used as reference electrode. All the solutions were deaerated by bubbling N_2 through them for 10 min before the current flew. Ppy films were grown by consecutive square waves of potential applied between -0.30 V (2 s) and 0.87 V (8 s) in 0.2 M pyrrole + 0.2 lithium perchlorate acetonitrile solution (with a 2% of water content). Ppy thin films of about $0.22 \text{ }\mu\text{m}$ and $35 \text{ }\mu\text{g}$, showing electrochromic properties (yellow in undoped state and blue dark after oxidation) were obtained.

2.1.2. Chemical Ppy

Pyrrole (98%) and additives were purchased from Sigma–Aldrich and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ from Panreac. All of them were used as received. The chemical oxidative polymerization of pyrrole was carried out as previously described in the literature [29,30].

As an example, in a typical synthesis of Ppy, a solution was prepared by mixing *N*-(2-hydroxyethyl)-2-pyrrolidinone (12.5 ml, 110 mmol) and water (37.5 ml) in a 250 ml flask at room temperature. To this solution, iron(III) chloride (47.3 g, 175 mmol) was slowly added and after 30 min of stirring, the solution was cooled down to $-5 \text{ }^\circ\text{C}$. Then, pyrrole (1.2 ml, 17.3 mmol) was poured in a single portion under vigorous stirring. After a reaction time of 30 min, the resulting black Ppy precipitate was filtered, repeatedly washed with methanol and finally dried under dynamic vacuum until constant weight.

2.2. Reduction of doped Ppy

2.2.1. Electrochemical reduction

After electrogeneration, each polymer-coated electrode was rinsed with distilled water and transferred into 0.2 M lithium perchlorate water solutions, in which electrochemical control would take place. The electrochemical reduction of the electrochemically generated Ppy films was carried out using a Voltalab 21 potentiostat–galvanostat. The doped Ppy electrode was reduced at constant current up to -0.8 V versus SCE.

2.2.2. Chemical reduction

In order to find the best reducing agent, distilled water solutions of the following reductants were used: sodium hydrosulfite ($\text{Na}_2\text{S}_2\text{O}_4$), sodium hydrogensulfite ($\text{Na}_2\text{S}_2\text{O}_5$), hydroxymethanesulfinic acid monosodium salt ($\text{HOCH}_2\text{SOONa}$), sodium borohydride (NaBH_4), formamidinesulfinic acid ($\text{H}_2\text{NCNHSO}_2\text{H}$), stannous chloride (SnCl_2) and hydrazine (N_2H_4). The solutions were deaerated by bubbling N_2 through them for 10 min before the current flow to avoid the oxidation of the undoped Ppy on air. All chemical compounds used in chemical reduction were purchased from Aldrich Co. with at least 98% purity and used without further purification. Reduction was carried out at room temperature.

2.3. Cell assembly and characterization

One hundred and seventy to 180 mg of chemical Ppy was used as the positive electrode (cathode); electrodes were prepared by pressing against aluminium current collector at 40 bar for 5 min. A solution of LiPF_6 in EC/DC (50:50, v/v) (Merck) is used as electrolyte. The graphite electrodes were obtained by a spray technique on a copper foil a mixture of commercial graphite (Timcal SLE-SLX 500) using a polyvinylidene fluoride PVDF (Atofina) as binder and *n*-methylpyrrolidone as the carrier solvent. They were used in the cells in their non-lithiated state. They were cut in $4.5 \text{ cm} \times 1.9 \text{ cm}$ electrodes supporting 40 mg active mass. A micro glass fibre (Albet) is used as separator. The cell was assembled in a dry box (M-Braun Lab Master 130). The prototype was sealed using thermofusible aluminium paper. Electrochemical studies of the final prototypes were per-

formed 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 (versus Li) range.

3. Results and discussion

In order to analyse the reducing capacity of different reductants a first approach was done by using an electrochemically synthesized thin Ppy film, where the electrochromic properties of the material can be used as reduction criteria (polymer colour changes depending in the oxidation state, blue in oxidized state and yellow in undoped state).

3.1. Screening of reductant

A similar procedure is used in all cases to know the reducing strength of different reductants and how they affect to the electroactivity of the conducting polymer. This procedure is outlined in Table 1.

After the electrochemical synthesis of Ppy on a platinum electrode (step I), the full stored charge is electrochemically measured performing a charge–discharge cycle at constant current of 0.3 mA between the reversible potentials of Ppy: -0.8 and 0.4 V versus SCE (steps II and III).

The charge obtained during this electrochemical reduction between the defined potentials is Q_1 and is assumed to be only the polymer reduction charge, where no electrochemical degradation reaction occurs. After electrochemical reoxidation, the film is chemically reduced (step IV) and a change in the colour from blue (oxidized Ppy) to lighter colour (undoped Ppy) is visualized. In order to properly compare the results, the reduction process is completed until -0.8 V versus SCE (step V) at constant current. The remaining charge measured is Q_2 and so, the difference between Q_1 and Q_2 values shows the charge that has been reduced chemically.

Finally, a third discharge capacity is electrochemically measured (step VII) obtaining Q_3 during reduction process, in order to check if the chemical reduction has affected the film causing any kind of degradation in the polymer, leading to a decrease in the ability to store charge.

In Fig. 1, the evolution of the oxidation state of the Ppy during the previously described process is shown.

Table 1
Experimental method to quantify the chemically reduced charge and percentage of degradation of electrochemical Ppy films

Step	Method	Process	Result
I	Electrochemical	Oxidation	Synthesis of Ppy
II	Electrochemical	Reduction	Measure Q_1
III	Electrochemical	Oxidation	Return to initial conditions
IV	Chemical	Reduction	Change colour
V	Electrochemical	Reduction (complementary)	Measure Q_2
VI	Electrochemical	Oxidation	Return to initial conditions
VII	Electrochemical	Reduction	Measure Q_3
VIII	Electrochemical	Oxidation	Return to initial conditions

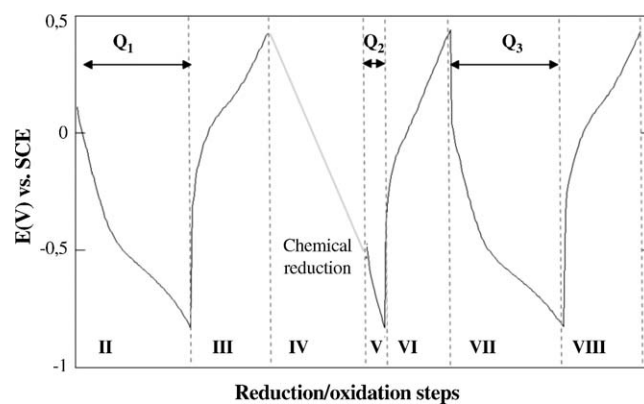


Fig. 1. Cronopotentiograms performed to a electrochemically synthesized Ppy film between 0.4 and -0.8 V vs. SCE at a constant current of 0.3 mA in 0.1 M LiClO_4 water solution. Different steps of measure procedure and Q_1 , Q_2 and Q_3 values are shown in the graph.

Two parameters are used to quantify the chemically reduced charge (Eq. (2)) and the degradation (Eq. (3)) using the electrochemically reduced charges (Q_1 , Q_2 and Q_3),

$$\% \text{ of reduction} = \frac{Q_1 - Q_2}{Q_1} \times 100 \quad (2)$$

$$\% \text{ of degradation} = \frac{Q_1 - Q_3}{Q_1} \times 100 \quad (3)$$

All these results are shown in Table 2, where the chemically reduced charge and degradation are present in percentage together with the colour change shown after chemical reduction. Reductant concentration was the same in all cases (0.1 M). The criteria chosen from preliminary experiments was to use the lowest possible concentration in order to avoid degradation of the polymer, but high enough to reduce the electrodeposited polymer. Since the thickness of the electrochemically generated film was very low, short immersion times were enough to check the effectiveness of the reducing agent.

As is shown in the Table 2, a good correlation between the percentage of reduced polymer and the reached colour is obtained. The colour of the completely undoped Ppy is yellow, thus, as the chemical reduction takes place, the colour of the polymer would pass from blue to yellow. Less reduced polymers will show darker colours (yellow–dark yellow–green yellow–light green). On the other hand, sodium borohydride gives the best results in the chemical reduction of doped Ppy, reducing about the 85% of the polymer charge. In most cases, the degradation process due to the effect of the chemical reduction could be considered not significant as Q_1 is similar to Q_3 .

3.2. Chemical reduction of chemically synthesized polypyrrole with NaBH_4

The next step will be therefore to study the reduction conditions in order to optimize time and reductant concentration. NaBH_4 was chosen as the most promising of the reducing agent tested and new experiments were performed to analyse the optimum concentration and duration of the treatment. In order to

Table 2
Percentages of chemically undoped polymer, degraded polymer and the colour of electrochemical Ppy film after being chemically reduced with different reagents

Reductant (0.1 M)	Q_1 (mC)	Q_2 (mC)	Q_3 (mC)	% Chem. reduced	% Degradation	Colour after chem. reduced
Sodium borohydride	1260	200	1230	85	2.4	Light yellow
Formamidinesulfonic acid	1420	595	1300	58	4.9	Dark yellow
Hydroxymethanesulfonic acid monosodium	1350	690	1320	49	2.2	Green yellow
Sodium hydrogensulfite	1190	730	1185	39	0.4	Green yellow
Hydrazine	1280	860	1220	32	4.7	Light green
Sodium hydrosulfite	1220	830	1230	31	−0.8	Light green
Stannous chloride	1350	1060	1340	21	0.7	Green

Table 3
Percentages of undoped polymer and degraded polymer of chemical Ppy after being chemically reduced with NaBH_4 at different concentrations and treatment times

Concentration (M)	Time (min)	Q_1 (mC)	Q_2 (mC)	Q_3 (mC)	% Chem. reduced	% Degradation
0.05	35	1280	590	1210	54	5
0.05	45	1310	310	1100	76	16
0.1	10	1280	860	1220	33	4.5
0.1	20	1340	690	1320	49	1.5
0.1	25	1320	595	1280	55	3
0.1	35	1260	200	1230	85	2.4
0.1	45	1220	190	1050	85	14
0.1	60	1400	50	350	96	75
0.2	25	1340	420	1100	67	18
0.2	35	1270	90	400	93	67

further investigate the industrial feasibility of this reduction procedure, a chemically polymerized Ppy rather than electrochemically synthesized one is used due to its higher feasibility from industrial point of view. The Ppy obtained by chemical polymerization is a black powder. This polymer is cleaned and dried before fixing it over an inert oil-graphite paste electrode [31]. The quantity of the used polymer was always the same (10 mg). These electrodes were introduced in different concentrations of NaBH_4 water solutions for different periods of time, and then they were washed with water and finally reduced electrochemically to quantify the remaining charge after chemical reduction. The method to obtain the percentage of chemically undoped polymer and degraded polymer is the same as Table 1 and these percentages, together with the Q_1 , Q_2 and Q_3 values, are shown in Table 3.

As is shown in Table 3, in all studied concentrations, an increase in the percentage of undoped polymer is observed by increasing the reduction time. Values near to 100% are obtained when the polymer is reduced during 60 min in 0.1 M solution. Almost half of this time is needed when the concentration is doubled to 0.2 M. However, when a large amount of chemical Ppy has to be undoped and therefore longer treatment times are required, degradation reactions should be taken into account. This is clearly shown in Fig. 2, where the evolution of the percentages of undoped polymer and polymer degradation against chemical reduction time in 0.1 M solution is represented. When the chemical reduction time exceeds 35 min, significant degradation phenomena occur in the electrode, leading to the polymer electroactivity loss. Similar behaviour is observed in 0.2 M starting above 25 min of treatment.

In the chemical synthesis of Ppy different oxidizing agents (as FeCl_3 , HSO_4Na , ...) or additives are used; these products can be trapped in the polymer matrix during polymerization [32], and they can interfere in the later chemical reduction. Then, degradation can be associated to undesired reactions between the reductant and the oxidizing agent trapped in the polymer

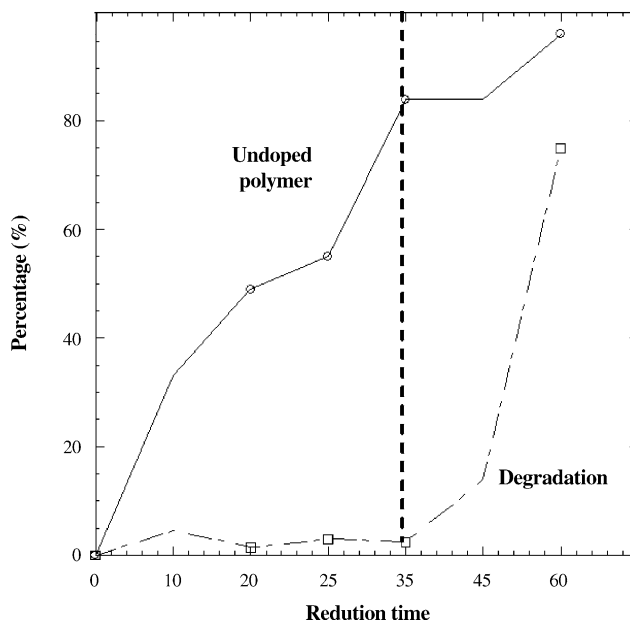


Fig. 2. Evolutions of the percentages of undoped polymer and polymer degradation against chemical reduction time in 0.1 M NaBH_4 water solution are represented.

matrix. Therefore, the best results are obtained in 0.1 M NaBH₄ water solution (5 mmol), and a treatment of 35 min.

3.3. Graphite–polypyrrole batteries

Different battery prototypes using Ppy as cathode have been described [15–25] in the literature. Using a thin lithium electrode as anode, an experimental specific energy of 20–30 Wh kg⁻¹ was obtained, being 240 Wh kg⁻¹ [33] (versus lithium) its theoretical value. These prototypes never have been commercialised, due to the use of lithium as anode in rechargeable batteries and the poor performance achieved. Scrosati et al. showed a battery using graphite as anode and electrochemical Ppy as cathode. A current density of 0.25 mA cm⁻² was applied to charge–discharge the battery. This kind of prototypes can be used in the field of microbatteries. However, with the chemical reduction method shown in this article it is possible to prepare cells having polymer electrodes with the similar mass per square centimetre to the commercial inorganic cathodes used in lithium-ion batteries [34], with the important advantage, from the industrial point of view, that no electrochemical process takes place before the cell assembling.

Two different Ppy/graphite prototypes (4.5 cm × 1.9 cm) were assembled using a chemically synthesized Ppy electrode as cathode, graphite as anode and a solution of LiPF₆ in EC/DC (50:50, v/v) as electrolyte (Fig. 3).

The first prototype had the Ppy electrode chemically reduced before assembling the cell. The Ppy electrode was introduced in 0.1 M NaBH₄ solution for 35 min. The chemically undoped Ppy was washed and dried under vacuum at 40 °C. Then, the cell is assembled with a graphite anode in the dry box having 40 mg on a copper electrode. The prototype is charged at a constant current of 68 mA (C/40). The evolution of the potential versus capacity during the first cycle of charge–discharge is shown in Fig. 4.

In the second prototype, the Ppy reduction process was electrochemically carried out for comparison purposes. Before reduction, the Ppy electrode was assembled with a thin lithium film in 4.5 cm × 1.9 cm cell as in Fig. 3. The doped Ppy is reduced applying consecutive potentials steps of 100 mV from 3.5 to 1.8 V versus Li (Fig. 5a). Once the Ppy is undoped (the electrode is in a discharged state), the cell is introduced again in



Fig. 3. Ppy/graphite battery prototype.

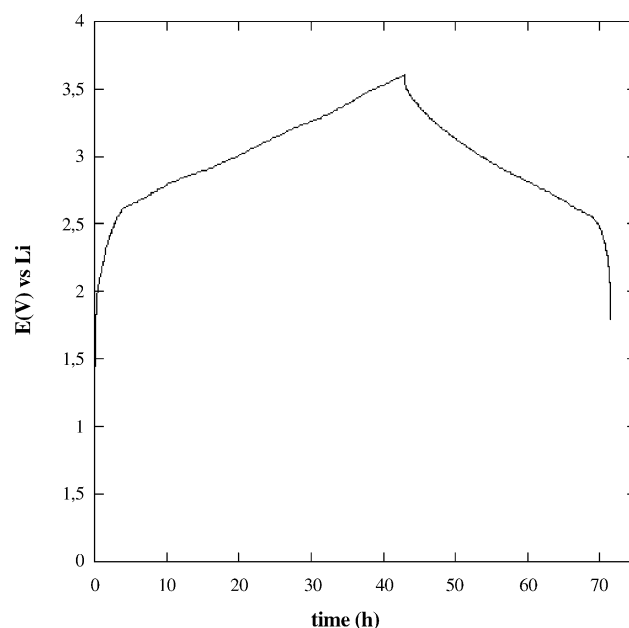


Fig. 4. Evolution of the first cycle of charge–discharge of the capacity vs. potential of a Ppy–graphite cell at 68 mA. In this case, the doped Ppy electrode is chemically reduced before the cell is assembled.

a dry box and the Ppy electrode (dark green) removed. Then it is assembled in a new battery against a graphite electrode. The cell is charged at constant current of 68 mA (with the aim of charge–discharge at C/40). The charge–discharge cycle is shown in Fig. 5b.

Figs. 4 and 5b show clearly the electrochemical behaviour of the first charge–discharge cycle of graphite–Ppy dion battery assembled from undoped Ppy and fresh graphite. The potential increases showing a shoulder at 2 V versus Li related to the SEI layer formation [35–37] on graphite surface. Afterwards, the potential was gradually increased until 3.6 V versus Li according to the charge–discharge Ppy profile.

The main parameters of both prototypes are shown in Table 4.

Table 4 shows values of specific capacities and specific energies of a graphite–Ppy dion battery from previously undoped Ppy (chemical and electrochemically). Values are defined only taking into account the mass of active materials. Also, the specific capacity for anode and cathode electrodes is shown. Comparing with literature acceptable performances are obtained for the graphite electrodes as it was expected, however, with lower values being achieved for Ppy electrodes. This may be associated to the lower electronic conductivities of chemically synthesized Ppy compared to the electrochemical deposition on conducting substrates. Both prototypes have similar electrochemical characteristics, which show the effectiveness of the chemical reduction to prepare Ppy batteries. However, the specific energy and capacity observed are still far from the theoretical values for Ppy electrode (300 Wh kg⁻¹) or values for inorganic oxide electrodes (450 Wh kg⁻¹ for LiCoO₂) [38]. Nevertheless, these are promising values and the chemical reduction method explained in this article is an additional step to the use of Ppy as a commercial electrode. More work must be done in order to find new chemical synthetic methods or new polymers that can improve these

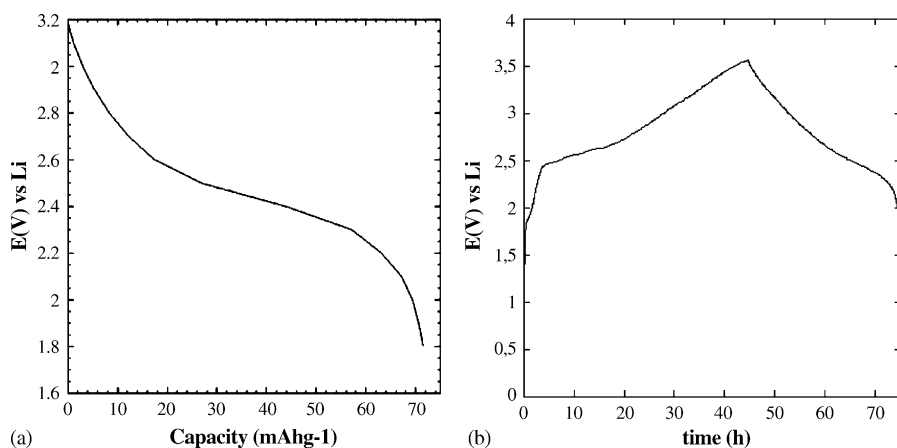


Fig. 5. (a) Electrochemical reduction of doped Ppy electrode before the cell is assembled by applying consecutive potential steps of 100 mV from 3.5 to 1.8 V vs. Li. (b) Evolution of the first cycle of charge-discharge of the capacity vs. potential of a Ppy-graphite cell at 68 mA.

Table 4

Specific energy and specific capacity related to polypyrrole mass, graphite mass obtained in the chemically and electrochemically reduced prototypes

	Ppy mass (mg)	Graphite mass (mg)	Graphite + Ppy mass (mg)	Ppy (mAh g ⁻¹)	Graphite (mAh g ⁻¹)	Graphite + Ppy	
						mAh g ⁻¹	Wh kg ⁻¹
Chemically reduced prototype	182	41	223	63	276	51	138
Electrochemically reduced prototype	171	40	211	65	280	53	144

still low energy values. In any case, the lower energy disadvantage can be counterbalanced with the flexibility of the polymer nature, the low weight, low cost and the environmental friendliness.

4. Conclusions

In this paper a chemical reduction method of Ppy has been developed, using different reductants in order to choose the most appropriate one. Best results were obtained with NaBH₄, capable of reducing about the 85% of the polymer charge with minimal degradation. This method opens a new manufacturing way for conducting polymer applications where an undoped polymer is needed. One of these applications could be the use of Ppy electrode in lithium-ion batteries where an undoped polymer is needed as electrode: it has been demonstrated that Li ion batteries can reach about 140 Wh kg⁻¹ of specific energy using Ppy as a cathode (50% of the theoretical value). The developed chemical reduction would be a low cost and easy process increasing the industrialization possibilities of the conducting polymers.

Acknowledgments

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