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Performance of polyaniline electrosynthesized in the presence of trichloroacetic acid as a battery cathode

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Abstract

In this study, the charge–discharge characteristics of polyaniline films used as cathodes in a lithium battery were determined. The polymer films were synthesized in a propylene carbonate medium in the presence of trichloroacetic acid. The discharge capacity and the coulombic efficiency observed for polyaniline thin films were 107 A h kg⁻¹ and 97.5%, respectively. For thick polyaniline films the values obtained were 82 A h kg⁻¹ and 95.0%, for the discharge capacity and coulombic efficiency, respectively. These values were stable after the seventh charge–discharge cycle. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Lithium battery; Conducting polymers; Polyaniline; Trichloroacetic acid; Propylene carbonate

1. Introduction

The development of new cathodic materials for rechargeable lithium batteries is necessary in order to minimize the processes responsible for the charge–discharge capacity loss occurring when these devices are submitted to multiple charge–discharge cycles. The use of polyaniline (PAni) as electrode material for batteries presents interesting applied results because it shows a high discharge capacity (ca. 95 A h kg⁻¹ [1–3]) as well as high coulombic efficiency [1–7] associated with very high electrochemical stability observed during multiple charge–discharge cycles. Spila et al. [8] investigated the possibility of fabricating solid state, heavy-metal free lithium-ion batteries by using gel electrolyte cells with polypyrrole and polyaniline cathodes. In the case of PAni cathodes, the authors observed an initial sharp decrease in the specific capacity (first five cycles) followed by a tendency to stabilize at 30 A h kg⁻¹ [8].

To use the PAni in lithium battery charge–discharge assays, a synthesis method was developed in which the polymer films were obtained in a propylene carbonate (PC) medium [8] which is the medium used for the charge–discharge assays. In this case, the basic requirements

for a good electrolytic solution are satisfied by the presence of lithium perchlorate or another lithium salt [9]. However, the major problem in working with PC in the presence of acids is solvent hydrolysis. The utilization of strong mineral acids, such as hydrochloric and perchloric acids, results in the addition of a considerable amount of water. Another important requirement is the acid strength, because it needs to have power enough to promote the proton transfer to the PAni, in order to enable the formation of an electroactive polymer.

Osaka et al. [4] performed the electrochemical polymerization of PAni in PC medium in the presence of trifluoroacetic acid (TFA) and they observed that electrochemically active films were formed when the ratio of aniline monomer to acid was equal or less than 1:2. The authors [4] concluded that to obtain electroactive PAni films from PC solution also requires the presence of protons from an organic acid whose acidity is as high as that of TFA. In a previous work [10] electroactive PAni films were electropolymerized in propylene carbonate medium in the presence of 1.5 mol l⁻¹ trichloroacetic acid (TCA) and LiClO₄ as supporting electrolyte. The use of TCA was justified because it can be obtained with a small amount of water and that does not degrade the solvent. In addition, the authors observed that these films have a spongy structure and they detected perchlorate ions, from the electrolyte used in the electrosynthesis, incorporated into the matrix [10].

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Considering that electroactive PANi films can be electropolymerized in the presence of TCA, whose acidity is lower than for trifluoroacetic acid ($K_{\text{HA}}(\text{TFA}) = 4.05 \times 10^{-7}$ and $K_{\text{HA}}(\text{TCA}) = 7.75 \times 10^{-8}$ [11]), the aim of this work is to analyze the performance of these PANi films as cathodes for lithium batteries. In addition, considerations of the influence of the thickness and/or amount of inactive material in the film behavior are presented.

2. Experimental

The electrochemical synthesis of PANi was carried out using cyclic voltammetry in propylene carbonate medium in the presence of 1.5 mol l^{-1} TCA, as described elsewhere [10]. The charge–discharge assays were performed in a dry box under an argon atmosphere at room temperature (25 ± 2)°C with a potentiostat/galvanostat 263 (EG&G/PARC) controlled by the software M270 (EG&G/PARC). A one-compartment glass cell was used with a reference electrode (Li/Li^+), consisting of a metallic lithium wire immersed in propylene carbonate containing 1 mol l^{-1} LiClO_4 , a metallic lithium wire as auxiliary electrode and a Pt/PANi as the working electrode. Two working electrodes were tested: one containing 0.13 mg cm^{-2} of PANi (thin film) and another with 1.42 mg cm^{-2} of PANi (thick film).

The charge–discharge assays were carried out at $20 \mu\text{A cm}^{-2}$ in a propylene carbonate solution containing 1 mol l^{-1} LiClO_4 . Both films were charged until a potential value equal to 3.8 V and discharged to a potential of 2.5 V. Each charge–discharge assay involved 12 cycles and cyclic voltammograms were taken at 5 mV s^{-1} before and after each assay.

3. Results and discussion

In order to evaluate the usefulness of the PANi films electrosynthesized in PC medium containing TCA and LiClO_4 , as battery cathodes, two electrodes covered with different amounts of polymer were used. The micrographs for thin and thick PANi films are shown in Fig. 1. It can be observed that both films present a spongy structure in which it is not possible to distinguish fibrillar nor globular characteristics with the magnification used. However, the surface of the thick film is much more homogeneous than the thin one. Although holes could be seen in the thin film, the metallic substrate was not exposed. It is well known that the PANi film morphology depends on the specific electrochemical conditions used for its growth such as the solvent nature, supporting electrolyte, electrical conditions (potentiostatic or galvanostatic mode), potential range, etc. [1]. Several authors [12,13] described the PANi film formation as starting from a compact globular structure, after which porous fibrous structures are formed. On the other hand, soft and spongy PANi structures have also been reported for

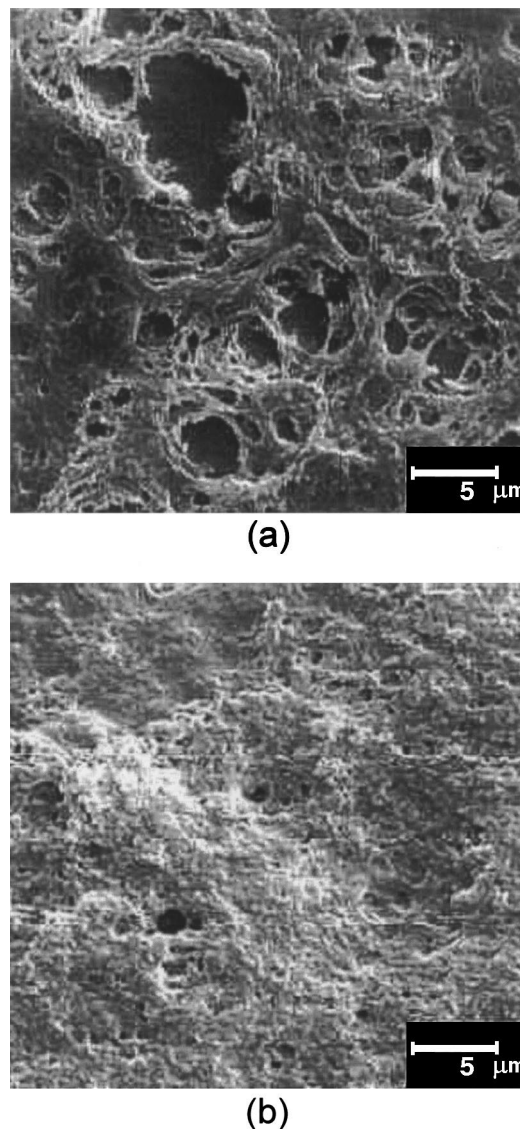


Fig. 1. Scanning electron micrographs of PANi, in the emeraldine salt oxidation state, electrosynthesized on platinum from a solution containing: 0.25 mol l^{-1} aniline, 0.5 mol l^{-1} LiClO_4 and 1.5 mol l^{-1} TCA in propylene carbonate medium; (a) thin and (b) thick film.

very thick films growth at constant current density [14]. In the present study, quite similar micrographs were found for PANi prepared on platinum substrates by the potential sweep method from propylene carbonate solution containing only aniline tetrafluoroborate [3]. It is very important to mention that the film morphology observed in the present work is different from that, globular, observed for PANi synthesized in aqueous medium in the presence of TCA and LiClO_4 . These morphological differences are an effect of the solvent nature, i.e. a consequence of the hydrogen bonds occurring in aqueous medium that interferes in the interaction between the chains. This kind of interaction is absent in the case of PC which is a typical example of a non-associated solvent.

In Fig. 2 the charge–discharge cycles for both kinds of PANi electrodes are shown. In the case of the thin film

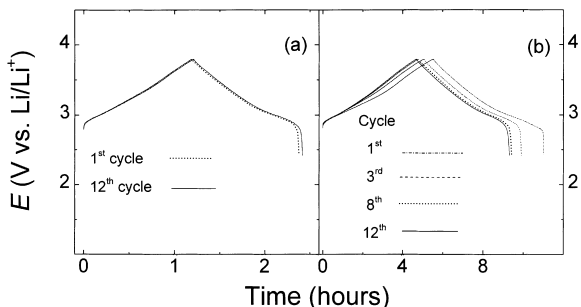


Fig. 2. Charge–discharge cycles of (a) thin and (b) thick PANi film in propylene carbonate solution containing $1 \text{ mol l}^{-1} \text{ LiClO}_4$; current density: $20 \mu\text{A cm}^{-2}$. The PANi films were charged at 3.8 V and discharged at 2.5 V. The corresponding cycle is indicated in the figure.

(Fig. 2a) one can observe that there is only a small increase of the discharge period when the number of cycles increases. On the other hand, for the thick film (Fig. 2b) it is possible to observe a decrease in the charge–discharge periods up to the seventh cycle after which it stabilizes. A behavior similar to the thick film was already observed by Tsutsumi et al. [6] using a PANi–PSS (poly(*p*-styrenesulfonic acid)) cathode, i.e. the charge–discharge period decreases with the number of cycles.

The electrochemical behavior of both films can be seen by the results presented in Fig. 3, where cyclic voltammograms of the PANi films are shown before the first charge–discharge cycle and after a charge–discharge assay (12 cycles). In the case of thin film (Fig. 3a) the total charge variation is quite small when compared with that observed for the thick film (Fig. 3b). This behavior may be related with a structural rearrangement of the polymer film since during the electro-synthesis the incorporation of oligomers in the polymer film can occur. When submitted to a linear potential sweep in a PC solution containing LiClO_4 these oligomers have the tendency to oxidize irreversibly between 3.2 and 3.8 V

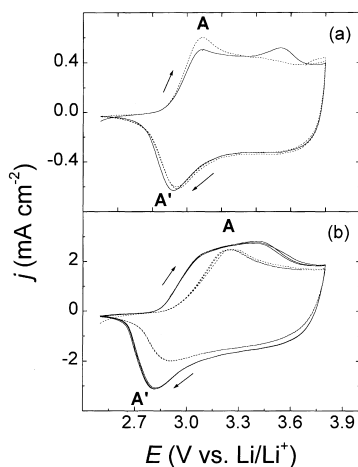


Fig. 3. Cyclic voltammograms of Pt/PANi in propylene carbonate solution containing $1.0 \text{ mol l}^{-1} \text{ LiClO}_4$. Scan rate: 5 mV s^{-1} ; potential range: 2.5–3.8 V; (a) thin; (b) thick film. Curves obtained (solid line) before and (dashed line) after the charge–discharge cycles.

versus Li/Li^+ , and, consequently the corresponding CVs will present the behavior shown in Fig. 3 (solid lines). This behavior is the typical electrochemical response found in the literature [5,15,16] with the first peak in the positive potential direction (peak A) associated with the transformation from the leucoemeraldine to the emeraldine oxidation state. Ryu et al. [17] attributed a similar peak as due to an oxidation process of Li^+ or $\text{PF}_6^-/\text{BF}_4^-$ doping and because the doping and dedoping processes are reversible, the shape of the peak doesn't change with cycling. In the present case, the peak shape changes with cycling and in addition, for the thick film (Fig. 3b) there is the occurrence of two peaks and a potential shift after the charge–discharge cycles. So, the appearance of the two peaks may be associated with a doping process occurring in parallel with the oligomer oxidation.

After all charge–discharge cycles, the polymer films showed the voltammetric features indicated in Fig. 3 by the dashed lines, which are expected for PANi in this medium. Assuming the incorporation of oligomers in the polymer, during these cycles their oxidation products will be removed from the polymeric matrix remaining in the electrolytic solution.

The dependence of the coulombic efficiency with the number of charge–discharge cycles is represented in Fig. 4 for both PANi films. The coulombic efficiency is high having a stable value of 97.5 and 95.0% for thin and thick films, respectively. For thin films, the result obtained for the first cycle (98.8%) is in agreement with that reported by Osaka et al. (98.5%) for PANi films grown in the presence of trifluoroacetic acid [4]. However, the authors performed only one charge–discharge cycle and they did not investigate the aging effect in the coulombic efficiency.

In Fig. 5, the dependence of the discharge capacity with the number of charge–discharge cycles is shown. It is interesting to observe that the discharge capacity value for the thin PANi film is higher than that for the thick film. For the thin PANi film the discharge capacity presented a stable value at 107 A h kg^{-1} , which is compatible with the value of $118.6 \text{ A h kg}^{-1}$ obtained by Echigo et al. [2]. On the other hand, for the thick PANi film the discharge capacity

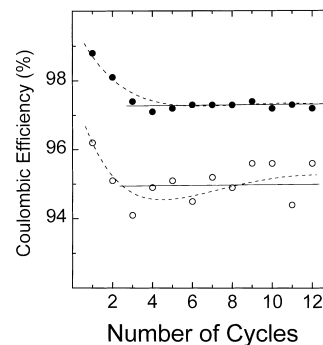


Fig. 4. Dependence of the coulombic efficiency with the number of charge–discharge cycles for the (●) thin and (○) thick PANi films in a propylene carbonate solution containing $1 \text{ mol l}^{-1} \text{ LiClO}_4$.

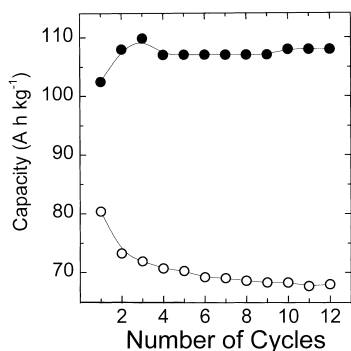


Fig. 5. Dependence of the discharge capacity with the number of charge–discharge cycles for the (●) thin and (○) thick PANi films in a propylene carbonate solution containing $1 \text{ mol l}^{-1} \text{ LiClO}_4$.

value was 70 A h kg^{-1} that is ca. 35% lower than that obtained for the thin PANi film. In spite of the low value, as compared to the thick film, this value is in good agreement with that obtained for PANi films chemically synthesized by Yang et al. [3] who determined discharge capacity values between 76 and 81 A h kg^{-1} . Both values obtained in the present work, calculated by using only the weight of the PANi, are in accordance with the range of discharge capacity values presented in the literature [1], which is between 65 and $118.6 \text{ A h kg}^{-1}$. It must be noted that, as mentioned by Novák et al. [1], the experimental specific charge or discharge capacity values are dependent on the polymer weight assumption. It means that, taking into account only the weight of the electroactive polymer, the value of the discharge capacity is much higher than if the weight of ions was also considered.

The difference observed in the discharge capacity of both modified electrodes used here may be explained by the amount of inactive material present in the film at the beginning of the charge–discharge cycles. It reinforces the supposition of oligomer incorporation, i.e. the thicker the PANi film the bigger will be the inactive mass or oligomer fraction. So, one can say that there is a strong influence of the film thickness in its charge–discharge characteristics for PANi film electrodes prepared electrochemically. This influence may be different for PANi films chemically synthesized. In this latter case, there is an additional step which is casting the polymer on the metallic substrate, for which the amount of polymer can change but the amount of oligomers can be, in general, reduced due to the preparation process.

4. Conclusions

The PANi films electrosynthesized on platinum substrates from PC solutions containing TCA and LiClO_4 present

discharge capacity and coulombic efficiency values strongly dependent on the PANi film thickness. The values of discharge capacity and coulombic efficiency were, respectively, 107 A h kg^{-1} and 97.5% for thin PANi film and 82 A h kg^{-1} and 95.0% for thick PANi film. These values were stable after seven charge–discharge cycles and comparable with those obtained for other PANi films electrosynthesized in PC medium in the presence, for instance, of trifluoroacetic acid and aniline tetrafluoroborate. However, it is important to mention that since TCA is weaker, less volatile and less corrosive than trifluoroacetic acid, the films obtained in TCA present more advantages for their application in lithium batteries.

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