

# Electrochemical Polymerization of Aniline in Phosphoric Acid

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**ABSTRACT:** The electrochemical synthesis of common conductive polymers such as polyaniline in phosphoric acid is a little different from that in other acidic media such as sulfuric acid. Electropolymerization in phosphoric acid is difficult, and this electrolyte medium is not applicable for this purpose. However, it is possible to overcome this problem by the addition of a small amount of sulfuric acid. In this case, the electropolymerization process can be successfully performed when the phosphate ion is doped. For instance, polyaniline films electrodeposited from an electrolyte solution of phosphoric acid have good stabilities and useful morphologies. Interestingly, phosphate doping results in the formation of nanostructures, whereas the polymer surface is macroscopically smooth. In an appropriate ratio, a mixed electrolyte of  $\text{H}_3\text{PO}_4$  and  $\text{H}_2\text{SO}_4$  can be used for the electropolymerization of aniline; thus,  $\text{H}_2\text{SO}_4$  acts as a required agent for successful polymer growth, and  $\text{H}_3\text{PO}_4$  acts as a doping agent. In this case, a small amount of sulfate is incorporated into the polymer matrix, which does not participate in the electrochemical insertion/extraction process. © 2006 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 44: 3304–3311, 2006

**Keywords:** conducting polymers; morphology; nanoheterogeneity; nanostructure; polyaniline

## INTRODUCTION

The electrochemical synthesis of conductive polymers is accompanied by the doping of counterions into the polymer network. Because the material properties of conductive polymers are mainly affected by their doping states,<sup>1–12</sup> it is of particular importance to choose an appropriate medium for electropolymerization to attain conductive polymers of desirable properties for various applications. One of the prototypes of conductive polymers is polyaniline,<sup>13–27</sup> which has a well-defined electropolymerization process. Indeed, its electrochemical polymerization serves as an ex-

cellent model for the study of electropolymerization processes.

Aniline can be easily oxidized in the presence of various supporting electrolytes. However, it should be taken into account that polyaniline has good conductivity only at low pHs. Thus, acidic media are appropriate candidates for the electrochemical synthesis of polyaniline. In this direction, various acids have been employed for this purpose.<sup>22–27</sup> Among the simple inorganic acids, phosphoric acid is a common example, but less attention has been paid to it for the purpose of electropolymerization. To our knowledge, there has been no direct report on the electropolymerization of aniline from a solution of phosphoric acid. This is due to the fact that electropolymerization is difficult to be performed in a medium of phosphoric acid in comparison with other acidic media. This means that less atten-

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tion has been paid to the doping of polyaniline (and generally conductive polymers) by phosphate ions. In this context, there are some reports on the doping of conductive polymers with phosphate esters.<sup>28–30</sup> A few reports have also been devoted to physical studies of polyaniline doped with phosphate. These studies are due to the advantageous properties of conductive polymers doped with phosphate.<sup>31–34</sup> However, it is difficult to prepare stable films of conductive polymers via electropolymerization, whereas electrochemical polymerization is an efficient approach for the synthesis of conductive polymers and, in some cases, is the best method for synthesis. Thus, it is of particular importance to incorporate phosphate ions into the polymer matrix in the course of electrochemical synthesis. In this work, we explain that although electropolymerization from a phosphoric acid electrolyte is not favorable, it is possible to design a successful electropolymerization process resulting in phosphate doping. In other words, we report a practical approach for the preparation of phosphate-doped polyaniline (and generally conductive polymers) via a simple electropolymerization process under the appropriate conditions.

## EXPERIMENTAL

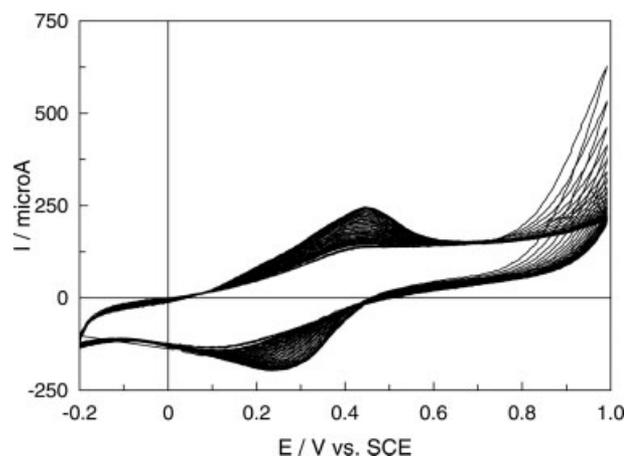
Electropolymerization processes were performed under potentiodynamic conditions with a conventional three-electrode electrochemical cell containing a platinum (Pt) electrode as the working electrode, a Pt sheet as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. The Pt electrode was carefully polished before the experiments and was heated on a flame to prevent any surface defects, as it has been recently discussed that such surface defects can significantly affect the electrochemical reaction and subsequently the polymer growth pathway.<sup>35</sup>

All electropolymerization processes were performed by potential cycling between  $-0.2$  and  $1.0$  V versus SCE at a scanning rate of  $100$  mV/s for 50 cycles. The concentration of aniline was constant ( $30$  mM) in all experiments, and the concentration of the acidic medium was varied. The synthesized electrodes were thoroughly washed with water to avoid the possible existence of electrolyte species on the polymer surface. Electrochemical studies of polyaniline films in supporting electrolytes were performed under

the same experimental conditions by potential cycling for 50 successive cycles. Electrochemical experiments were performed with a Princeton Applied Research potentiostat/galvanostat model 173 (PAR 173) equipped with a model 175 universal programmer in conjunction with CorrView software. A Philips XL 30 scanning electron microscope was employed for recording scanning electron microscopy (SEM) images and Energy Dispersive Analysis of X-ray (EDAX).

## RESULTS AND DISCUSSION

Figure 1 shows the electrochemical polymerization of aniline from a solution of  $0.1$  M  $\text{H}_3\text{PO}_4$ . A strong oxidation peak appears at high potentials and gradually decreases upon cycling. Because this is associated with aniline oxidation,<sup>16</sup> it can be concluded that the oxidation of aniline at the electrode surface is still active, even after several potential cycles, because the formation of a protective polyaniline film on the metallic substrate surface is expected. On the other hand, only a single peak associated with the polymer growth can be observed (Fig. 1). As a result of the low growth rate, it can be inferred that electropolymerization is not successful under these experimental conditions. A very thin polymer film deposited on the electrode surface is also unstable and can fall off quite easily. In conclusion, electropolymerization from the pure  $\text{H}_3\text{PO}_4$  electrolyte is not favorable, but the advantages of phosphate doping should not be

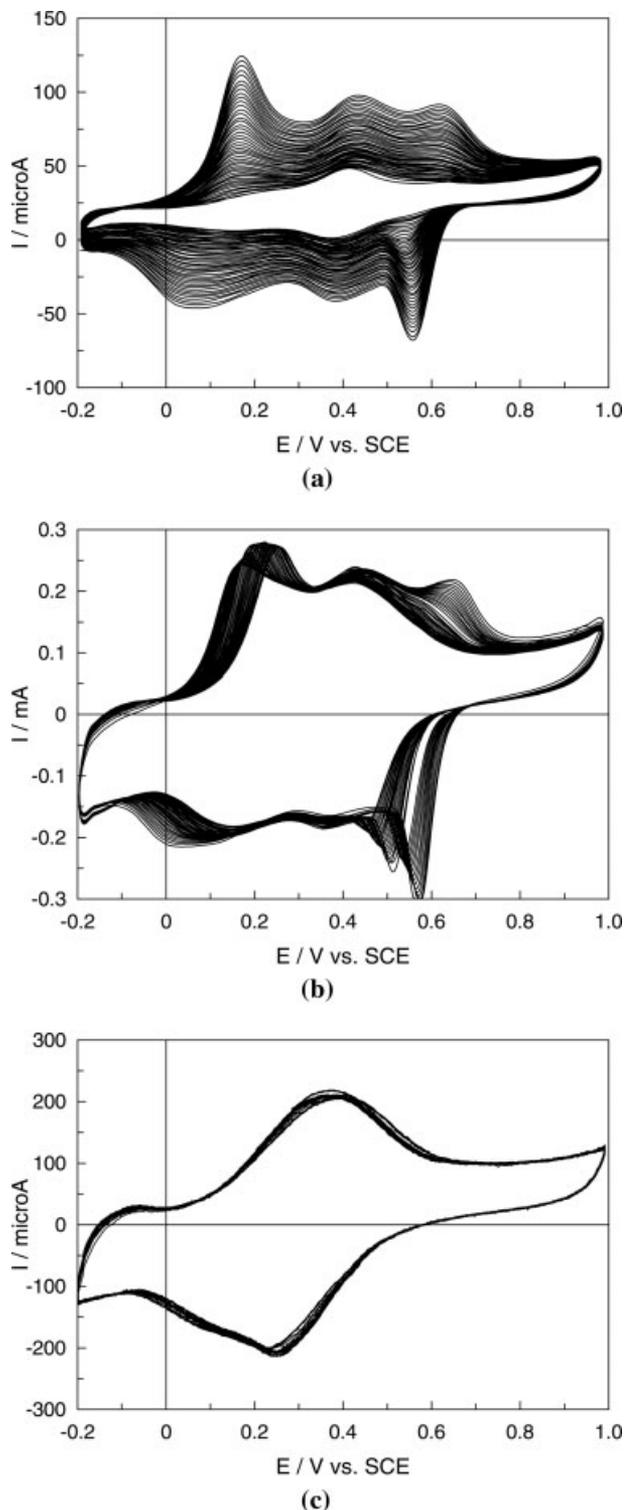


**Figure 1.** Potentiodynamic synthesis of polyaniline (as illustrated by plotting current  $I$  against potential  $E$ ) on a Pt electrode from a supporting electrolyte ( $0.1$  M  $\text{H}_3\text{PO}_4$ ). The concentration of aniline was  $30$  mM, and the scanning rate was  $100$  mV/s.

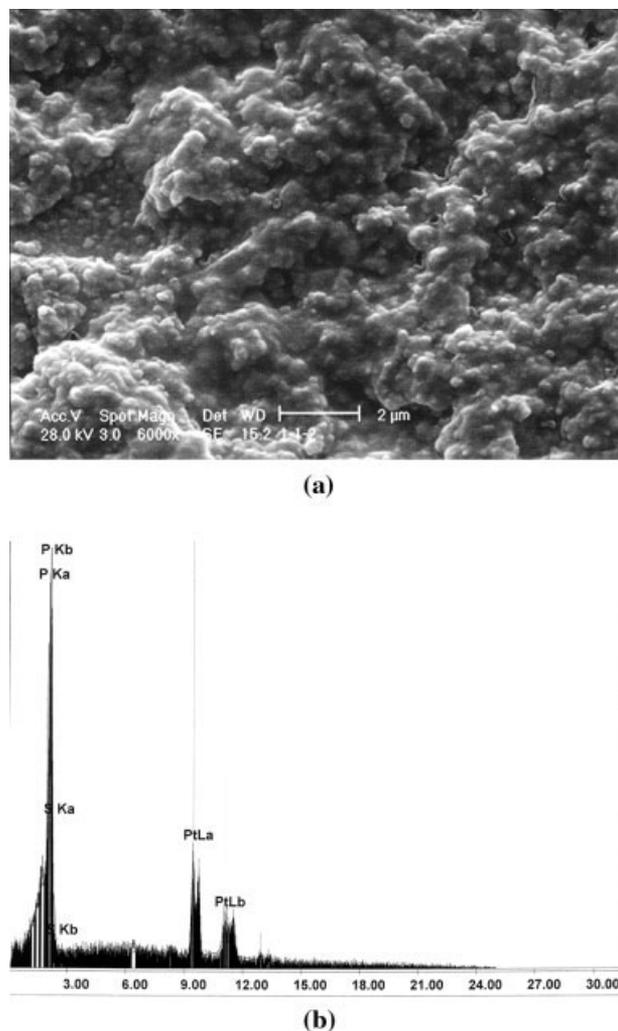
ignored. To gain this feature, we have attempted to assist the electropolymerization process by adding an active agent (e.g.,  $\text{H}_2\text{SO}_4$ ) in combination with the doping agent  $\text{H}_3\text{PO}_4$ . In this case, phosphate ions can be doped into the polymer structure, whereas  $\text{H}_2\text{SO}_4$  strengthens the electropolymerization to form a stable polymer film.

Figure 2(a) presents the potentiodynamic electropolymerization of aniline from a mixed medium of  $\text{H}_3\text{PO}_4$  and  $\text{H}_2\text{SO}_4$ . This indeed shows a well-defined electropolymerization as well as the pure  $\text{H}_2\text{SO}_4$  electrolyte. Interestingly, the oxidation peak is absent, and this indicates that the electrode surface is not active for aniline oxidation even during the first cycles. In other words, the rate of polymer growth is high enough to form a protective film immediately. Of course, a strong electropolymerization peak can be seen even during the first cycle. According to the medium employed for electropolymerization, the polyaniline should be doped with both phosphate and sulfate ions; thus, it should display electrochemical activity upon the insertion/extraction of sulfate or phosphate ions.

Figure 2(b,c) indicates the electrochemical behaviors of the polyaniline film in sulfuric and phosphoric acid solutions, respectively. Because both doping anions exist within the polymer structure, both can participate in an electrochemical system involving an insertion/extraction process. Because of the solid-state structure of the electroactive film, the insertion of a single anion instead of two different anions extracted from the polymer matrix is usually accompanied by a structural change of the polymer matrix and consequently the destruction of diffusion pathways within the polymer matrix.<sup>36</sup> Although the electrochemical insertion/extraction of sulfate ions is destructive and the polyaniline film loses its electrochemical activity [Fig. 2(b)], the polyaniline film can be easily cycled in a phosphoric acid solution as the insertion/extraction of phosphate ions is strongly reversible [Fig. 2(c)]. Moreover, the electrochemical activity of the polyaniline film with respect to the insertion/extraction of phosphate ions is accompanied by a single redox couple. This is of interest for electrochemical systems needing a constant potential, such as batteries. In such systems, the electroactive material should deliver a constant potential during the battery performance.<sup>37</sup> This single redox couple is characteristic of phosphate doping; therefore, redox peaks are those observed, though less successfully during



**Figure 2.** (a) Electropolymerization of aniline from a solution of 0.1 M  $\text{H}_3\text{PO}_4$  and 0.1 M  $\text{H}_2\text{SO}_4$ , (b) electrochemical behavior of a polyaniline film electrodeposited onto a Pt substrate in the  $\text{H}_2\text{SO}_4$  supporting electrolyte, and (c) electrochemical behavior of a polyaniline film electrodeposited onto a Pt substrate in the  $\text{H}_3\text{PO}_4$  supporting electrolyte. The number of cycles was 50 for all three cases.



**Figure 3.** (a) SEM image and (b) EDAX analysis of a polyaniline film prepared from a supporting electrolyte of 1:1  $\text{H}_3\text{PO}_4/\text{H}_2\text{SO}_4$ . The results of elemental analysis for phosphorus and sulfur indicated that the ratio of phosphorus to sulfur was 70.83:29.17 (atom %).

the electropolymerization of aniline from pure  $\text{H}_3\text{PO}_4$  (Fig. 1).

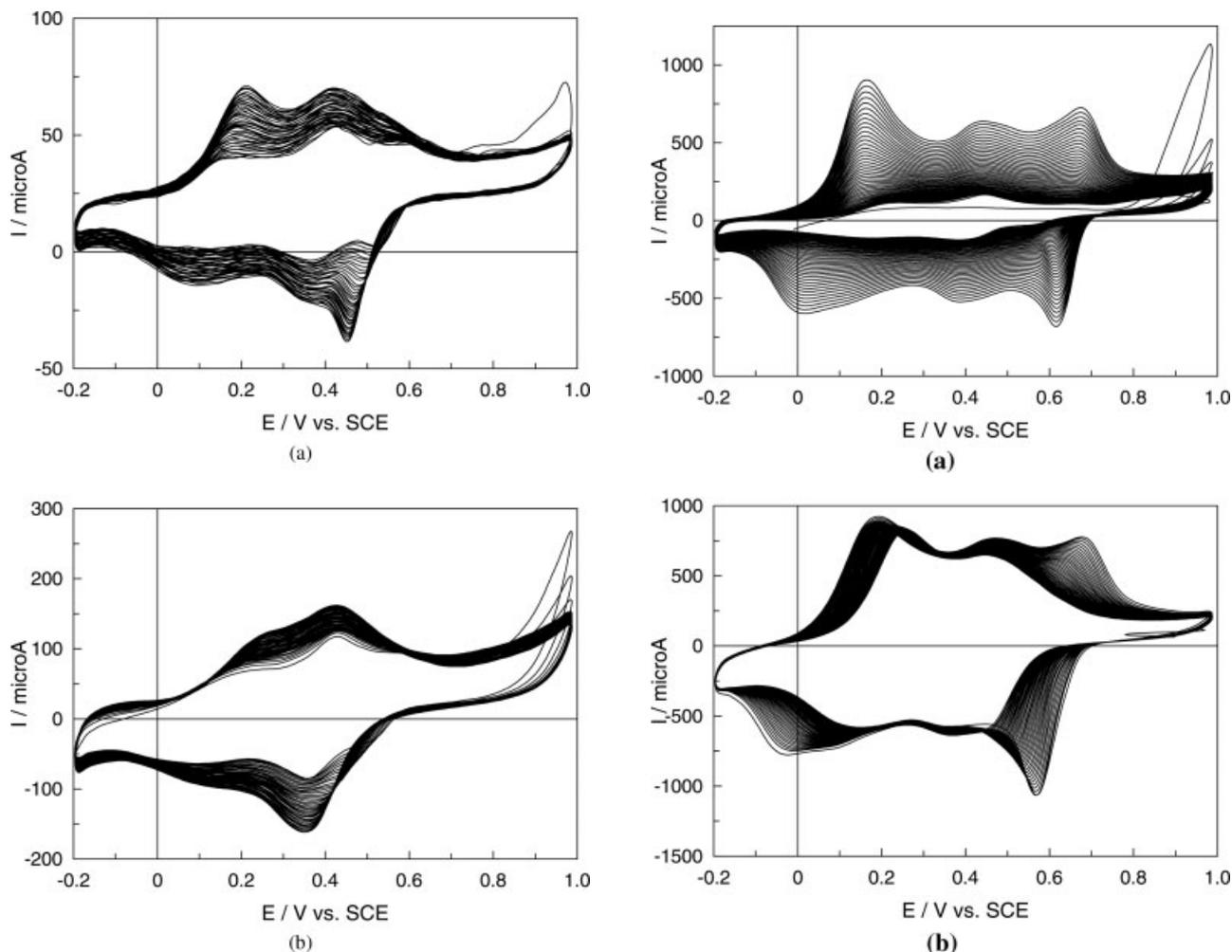
The polyaniline film prepared under the experimental conditions previously specified has a dense structure, as can be seen from the SEM image [Fig. 3(a)]. It is of particular interest for applied purposes such as electrochemical systems involving the diffusion of electroactive species.<sup>38</sup> Although it is smooth on a microscale, it has nanostructures. Of course, such nanostructures can be controlled by changes in the  $\text{H}_3\text{PO}_4$  concentration, as shown later. This is a noticeable advantage for diffusion processes occurring during the course of electrochemical activities of the polymer because diffusion processes just

needs appropriate channels on the nanoscale.<sup>39</sup> Elemental analysis of the polyaniline film obtained from the EDAX investigation revealed a phosphorus/sulfur relative atomic ratio of 70.83%:29.17%. This indicates that the doping anion is mainly phosphate rather than sulfate. In other words, the phosphate ion has a stronger tendency to incorporate into the polymer structure, probably because of its higher charge.

In the light of such results, the destructive electrochemical behavior of the polyaniline film in  $\text{H}_2\text{SO}_4$  [Fig. 2(b)] can be understood as doped phosphate ions, which should be replaced by sulfate ions from the electrolyte solution. However, such a problem is not applicable in the case of phosphate insertion/extraction as most doped anions are originally phosphate ions. Because insertion/extraction is not complete and only some of the doped anions will be extracted from the polymer matrix, it can be concluded that phosphate ions are the first ones to be extracted because their insertion/extraction is easier than that of sulfate ions. In fact, sulfate ions will not even be extracted from the polymer matrix during electrochemical insertion/extraction in the  $\text{H}_3\text{PO}_4$  electrolyte, as can be observed in Figure 2(c) and confirmed by the EDAX analysis of the cycled electrode (in fully charged or discharged states).

By the reduction of the  $\text{H}_2\text{SO}_4$  concentration, electropolymerization weakens, and the polymer growth pathway changes to that in pure  $\text{H}_3\text{PO}_4$ . Figure 4 depicts this effect, as the oxidation peak appears and the polymerization peaks tend to merge into a single redox couple when the  $\text{H}_2\text{SO}_4$  concentration decreases. This emphasizes the fact that  $\text{H}_3\text{PO}_4$  is not an appropriate supporting electrolyte for the electropolymerization of aniline and that the existence of  $\text{H}_2\text{SO}_4$  is mandatory for a successful electropolymerization of polyaniline doped with phosphate ions.

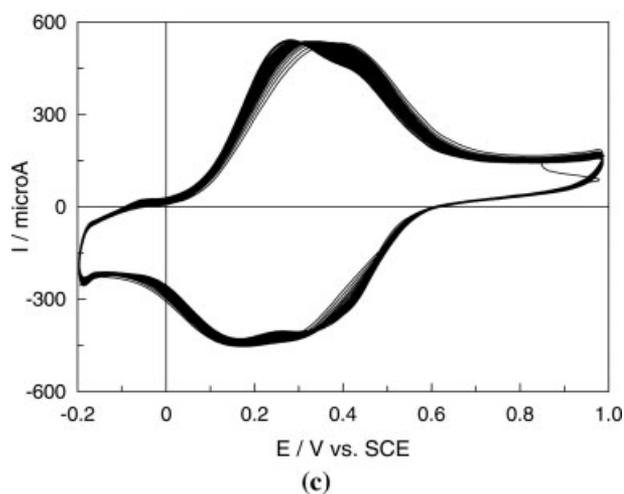
According to the aforementioned results, a certain amount of  $\text{H}_2\text{SO}_4$  is required to attain a successful electropolymerization process; thus, increasing the  $\text{H}_3\text{PO}_4/\text{H}_2\text{SO}_4$  ratio can increase the  $\text{H}_3\text{PO}_4$  concentration. Figure 5(a) shows the electropolymerization of aniline from a solution of 0.1 M  $\text{H}_2\text{SO}_4$  when the ratio of  $\text{H}_3\text{PO}_4$  to  $\text{H}_2\text{SO}_4$  is 5:1. It is obvious that potentiodynamic polymerization has a well-defined shape similar to that in pure  $\text{H}_2\text{SO}_4$  or that in 0.1 M  $\text{H}_3\text{PO}_4$  and 0.1 M  $\text{H}_2\text{SO}_4$  [Fig. 2(a)]. This well-defined behavior can be attributed to the existence of an appropriate amount of  $\text{H}_2\text{SO}_4$ . However, an excess amount of  $\text{H}_3\text{PO}_4$  also affects the electro-



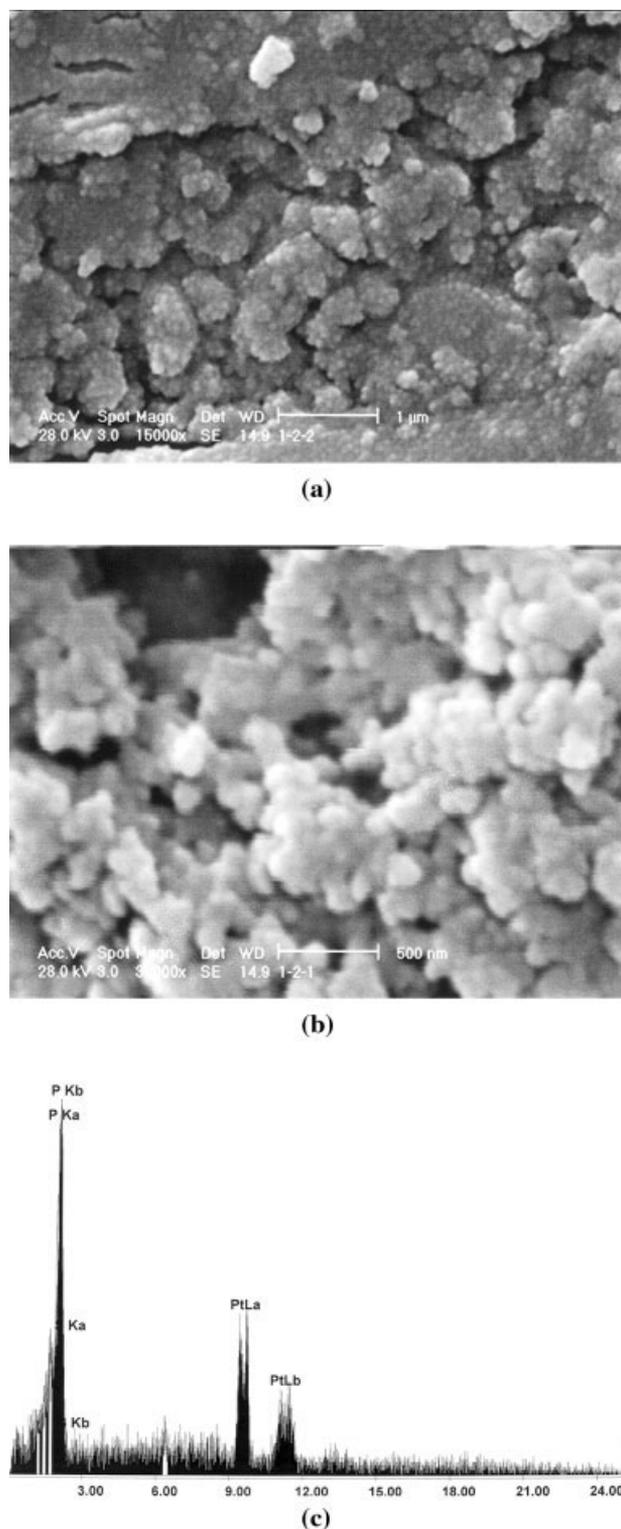
**Figure 4.** Electropolymerization of aniline from the  $\text{H}_3\text{PO}_4$  electrolyte in the presence of lower amounts of  $\text{H}_2\text{SO}_4$ : (a) 0.1 M  $\text{H}_3\text{PO}_4$  and 0.05 M  $\text{H}_2\text{SO}_4$  and (b) 0.1 M  $\text{H}_3\text{PO}_4$  and 0.025 M  $\text{H}_2\text{SO}_4$ .

polymerization. As can be seen, an oxidation peak at high potentials has appeared, although it is not very strong and disappears during the first cycles. The electrochemical behaviors of this polyaniline film in sulfuric acid and phosphoric acid are illustrated in Figure 5(b,c), respectively. The cyclability of the polyaniline film is slightly better in sulfuric acid and worse in phosphoric acid in comparison with that of the polyaniline film prepared in a solution of 0.1 M  $\text{H}_3\text{PO}_4$  and 0.1 M  $\text{H}_2\text{SO}_4$ . This effect is negligible, but its reason is discussed later.

SEM images of these polyaniline films indicate that the formation of the aforementioned nanostructure is more significant here [Fig. 6(a,b)]. This confirms the essential role of phosphoric acid in the formation of such nanostruc-



**Figure 5.** (a) Synthesis of polyaniline from a mixed electrolyte of 0.5 M  $\text{H}_3\text{PO}_4$  and 0.1 M  $\text{H}_2\text{SO}_4$  and (b,c) cyclic voltammetry of polyaniline films in the  $\text{H}_2\text{SO}_4$  and  $\text{H}_3\text{PO}_4$  supporting electrolytes, respectively, during 50 successive cycles. The scanning rate for all three cases was 100 mV/s.

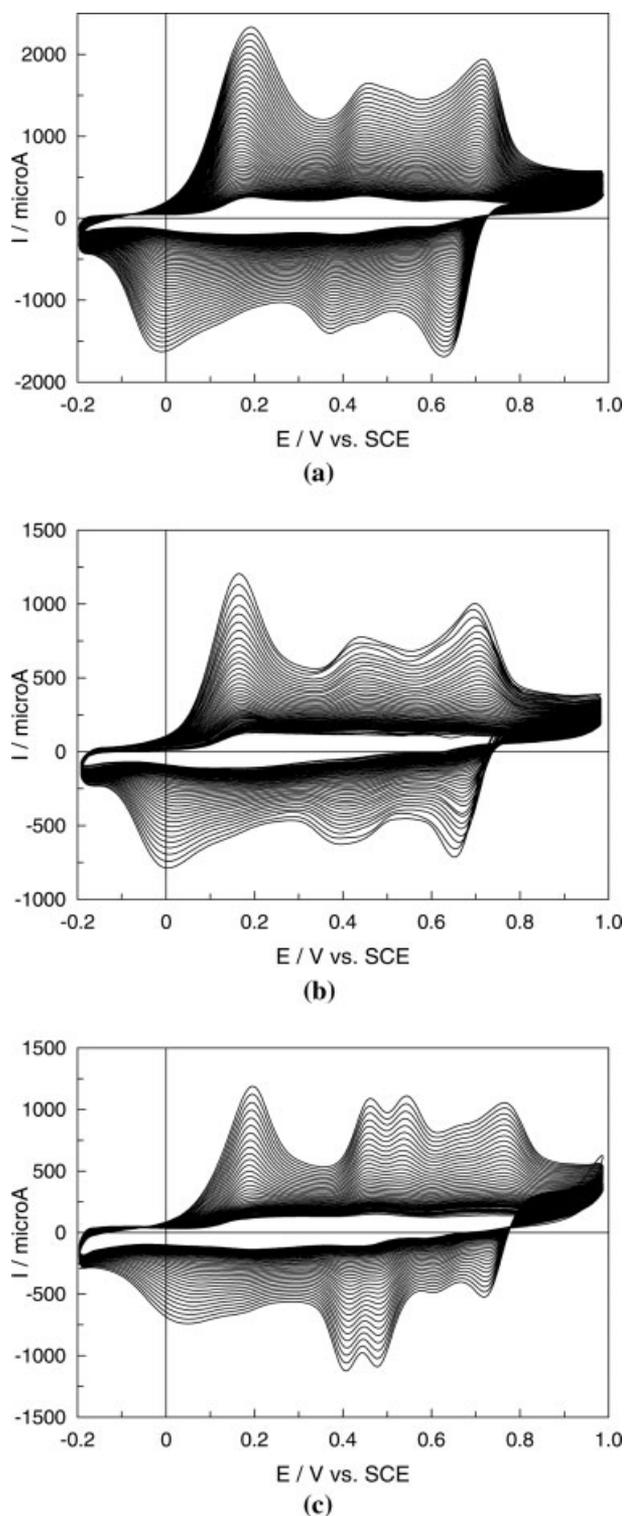


**Figure 6.** (a,b) SEM images of polyaniline synthesized in the presence of 0.5 M  $\text{H}_3\text{PO}_4$  and 0.1 M  $\text{H}_2\text{SO}_4$  and (c) EDAX analysis corresponding to the region illustrated in part a. The elemental composition was 66.23:33.77 phosphorus/sulfur (atom %).

tures. Interesting results have been obtained from the EDAX analysis of the latter polyaniline film [Fig. 6(c)]. In the presence of a higher ratio of  $\text{H}_3\text{PO}_4$  to  $\text{H}_2\text{SO}_4$ , the incorporation of higher amounts of phosphate ions rather than sulfate ions is probable, but the doping ratio is approximately 66.23%:33.77% phosphorus/sulfur in comparison with the former case (the polyaniline is synthesized in a ratio of 1:1). This indicates that the doping ratio of phosphate and sulfate ions is independent of the ratio of  $\text{H}_3\text{PO}_4$  to  $\text{H}_2\text{SO}_4$ . As stated previously, a certain amount of sulfuric acid is necessary for a successful electropolymerization; thus, a certain number of sulfate ions will be incorporated into the polymer structure over the course of electropolymerization. Because this amount of the sulfate dopant controls the electropolymerization process, an excess amount of phosphate ions cannot affect the incorporation of such essential sulfate ions.

According to these results, an excess amount of phosphoric acid is not favorable, and complete doping by phosphate ions (complete with respect to the insertion/extraction process) can be made by the electropolymerization in the ratio of 1:1  $\text{H}_3\text{PO}_4/\text{H}_2\text{SO}_4$ . However, we also studied the electropolymerization in concentrated  $\text{H}_3\text{PO}_4$  solutions. Potentiodynamic electropolymerizations of aniline from mixed solutions of  $\text{H}_3\text{PO}_4$  and  $\text{H}_2\text{SO}_4$  when the amount of  $\text{H}_3\text{PO}_4$  is extremely high are illustrated in Figure 7. Two significant effects, which are not critical to the polymerization process (i.e., the general form of electropolymerization is not changed), are observable. First, the oxidation peaks disappear, even though stronger peaks are expected, because of the existence of phosphoric acid. Second, the middle peak couple of the electropolymerization is divided into two thinner couples at a very high concentration of  $\text{H}_3\text{PO}_4$ .

The disappearance of the oxidation peaks can be attributed to the small amount of water in the solution. In fact, aniline oxidation at high potentials occurs in the presence of required ions such as phosphate. Because the acid concentration is extremely high, its ionization is weak, and there are no appropriate ions at the electrode surface for aniline oxidation. It is known that a certain amount of charge is passed before the electropolymerization process for the oxidation process, and this charge is related to both the electrolyte medium and electrode surface, as discussed for an active metal electrode in our previous work.<sup>24</sup>

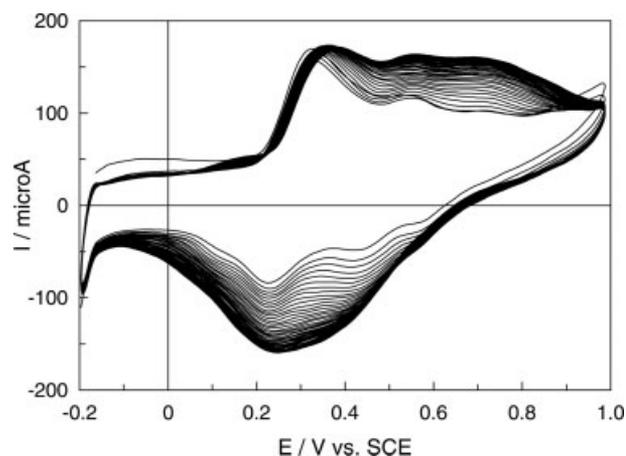


**Figure 7.** Electrochemical polymerization of aniline from mixed electrolytes of  $\text{H}_3\text{PO}_4$  and  $\text{H}_2\text{SO}_4$  in the presence of large amounts of  $\text{H}_3\text{PO}_4$ : (a) 1, (b) 2, and (c) 5 M. The concentration of  $\text{H}_2\text{SO}_4$  was constant: 0.1 M.

Electropolymerization in the absence of water, when the required amount of 0.1 M of  $\text{H}_2\text{SO}_4$  is available, indicates the requirement of water for ionization of the acids. It is obvious that the potentiodynamic curves of the electropolymerization process have a deformed shape (Fig. 8). On the other hand, a very thin film of polyaniline electrodeposited onto the substrate surface is extremely unstable and can be prone to mechanical breakdown.

## CONCLUSIONS

Although the electropolymerization of aniline in the presence of phosphoric acid is not successful, it is possible to use phosphoric acid as a doping agent to prepare polyaniline doped with phosphate ions. To this end, an appropriate acidic medium is required for the electropolymerization to proceed. Among the different acids examined for this purpose, sulfuric acid is the best. In this case, a certain number of sulfate ions will be incorporated into the polymer structure over the course of electropolymerization. However, these sulfate ions are not usually subject to the electrochemical insertion/extraction process, and generally it can be assumed that the polyaniline has been purely doped with phosphate ions. Polyaniline films doped with phosphate ions display superior electrochemical activity and stability. In addition, phosphate doping results in the formation of nanostructures, which are of interest for diffusion processes.



**Figure 8.** Electropolymerization of aniline from an acidic solution of 0.1 M  $\text{H}_2\text{SO}_4$  in concentrated  $\text{H}_3\text{PO}_4$  (water was not used). The electrolyte solution was 0.1 M  $\text{H}_2\text{SO}_4$  and 14.8 M  $\text{H}_3\text{PO}_4$ .

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