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A Novel Electrochemical Method for Enhancing the Conductivity of Polyaniline Solid Matrices in Preformed Films

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ABSTRACT: A fast, simple, and environmentally friendly new electrochemical method capable of enhancing the conductivity of a preformed polyaniline film has been found. Utilizing this method of electrochemical forcing pretreatment at a certain effective voltage, a polyaniline solid matrix can be made more conductive. For example, the conductivity of a preformed polyaniline film (as thick as 10 μm) can be easily enhanced by about an order of magnitude within a pretreatment time of only ca. 5 min. The UV−vis−NIR and ESR spectroscopic evidences indicated that the charge carriers in the polyaniline matrix are more delocalized after such electrochemical pretreatments. The results of CV studies indicated that the resultant polyaniline film has higher charge transport efficiency and a greater redox rate. Such phenomenon may be linked with a possible backbone conformational change, as induced by this novel electrochemical pretreatment, within the solid matrix of polyaniline film.

Introduction

Owing to their unique electrooptical properties and market potential, polyanilines are one of the recent focuses in the field of conducting polymer research.[1] Polyanilines have been demonstrated to be particularly useful in many applications, such as biosensors,[2] light-emitting diodes,[3] molecular devices,[4] conducting photoresists,[5] optical switches,[6] smart windows,[7] transistors,[8] rechargeable battery,[9] and anticorrosion.[10] For most of the applications, the conducting ability of polyaniline is one of the important and key properties.

It has been reported that a free-standing polyaniline film can be cast from 0.5 to 1 wt % solution of neutral polyaniline in *N*-methylpyrrolidinone (NMP). The conductivity of the resulting film was typically reported to be ca. 1−5 S/cm, after being doped with a protonic acid, e.g., HCl.[11] To further enhance the conductivity of polyaniline films, one can either subject a preformed polyaniline film (in the undoped form) to a mechanical stretching method [12] (often accompanied by a simultaneous heat treatment) or employ a chemical treatment method by casting a doped polyaniline film directly from a solution (whose preparation required a delicate mixing and dissolution process) of polyaniline containing a special primary dopant, e.g., camphorsulfonic acid, and a suitable solvent that can act as an effective secondary dopant, such as *m*-cresol.[13] Both methods were believed to help induce the formation of a more efficient matrix for charge transport, thus enhancing the conductivity of the films. The mechanical stretching approach is actually only useful for processing free-standing polyaniline films or fibers, whereas the chemical approach is especially useful for electric or electrooptical devices surfaces partially covered with polyaniline. For some important applications, such as anticorrosion coatings for automobiles and house appliances, a very useful approach is to grow polyaniline coating evenly on their diversely profiled surfaces via electrochemical means, similar to the electrodeposition of anticorrosion coatings traditionally used in the industry. However, such obtained polyaniline coatings often showed a regular bulk conductivity of less than ca. 5 S/cm, even when a good functional dopant (i.e., camphorsulfonic acid) was used, although MacDiarmid, Epstein, and co-workers have reported that the conductivity of a preformed thin (estimated to be ca. 100−200 nm thick by the reported UV−vis−NIR absorbance) polyaniline coating (having a functional primary dopant, e.g., camphorsulfonic acid) can also be improved via the treatment with the vapor of a good secondary dopant (i.e., *m*-cresol). But, such treatment had to be performed in a chamber filled with toxic *m*-cresol vapor (LD_{50} orally in rats: 2.02 g/kg)[14] for a long period (e.g., 2−17 h). Thus, there still lacks an environmental friendly and timesaving process to enhance the conductivity of electrochemically obtained polyaniline coatings for many existing and future potential applications.

We are reporting herewith a new electrochemical method that could be employed to enhance the conductivity of a preformed polyaniline film. This method works well in an aqueous solution and utilizes no organic solvents. It is very fast and works equally well for preformed thin or thick (ca. 10 μm) polyaniline film.

Experimental Section

The free-standing polyaniline film (ca. 10 μm thick) used for this work was cast from a solution of 0.48 wt % polyaniline emeraldine base in NMP, using a similar method as reported by MacDiarmid et al.[11] The polyaniline thin films on electrodes were grown in a three-electrode electrochemical cell, using platinum plates or ITO glass plates as the working electrode, a platinum plate as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. All the electrochemical polymerization reactions were controlled by a potentiostat (EG&G 273) under a constant current density of 13.3×10^{-6} A/cm^2 for 25 min in a 0.5 M H_2SO_4 aqueous solution that contained 0.1 M aniline. The thickness of the polyaniline electrode film thus obtained (of about 100 nm) was measured by SIMS (secondary ion mass spectroscopy) depth profiling and an α-step. Cyclic voltammograms of all resulted polyaniline films were performed on the same potentiostat in an aqueous solution of 0.5 M H_2SO_4. UV−vis−NIR spectra were performed basing on the polyaniline films on an ITO glass electrode, using a Hitachi U3501 spectrophotometer. The conductivity was measured by a typical 4-in-line probe method[13]

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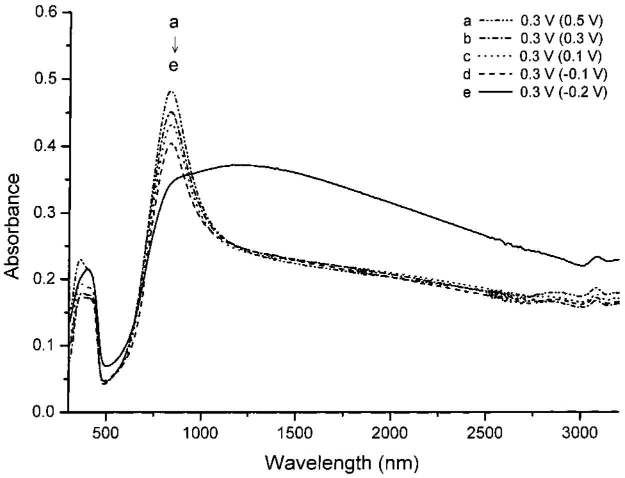

Figure 1. UV−vis−NIR spectra for the polyaniline films on ITO at an oxidation state of 0.3 V (vs SCE) in 0.5 M H_2SO_4 after a 10 min electrochemical pretreatment in 0.5 M H_2SO_4 at (a) 0.5, (b) 0.3, (c) 0.1, (d) −0.1, and (e) −0.2 V.

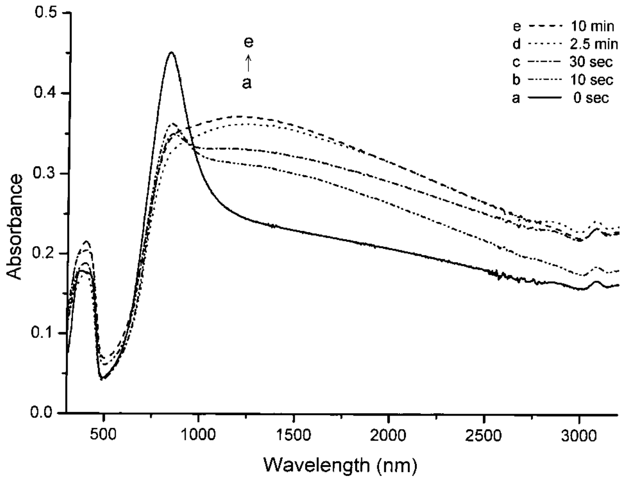

Figure 2. UV−vis−NIR spectra for polyaniline films on ITO at an oxidation state of 0.3 V (vs SCE) in 0.5 M H_2SO_4 after an electrochemical pretreatment in 0.5 M H_2SO_4 at −0.2 V for (a) 0 s, (b) 10 s, (c) 30 s, (d) 2.5 min, and (e) 10 min.

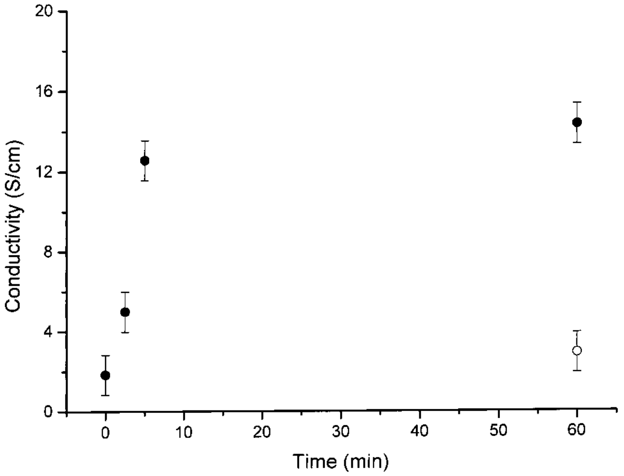

Figure 3. Conductivity of the polyaniline free-standing films (ca. 10 μm thick) after being electrochemical pretreated at −0.2 V (solid circle) for 0, 2.5, 5, and 60 min and at −0.1 V (open circle) for 60 min.

after the sample films were dried under dynamic vacuum for overnight. ESR spectra were obtained using a Bruker EMX-10 X-band (9.8 GHz) spectrometer with DPPH (α,α′-diphenyl-β-picrylhydrazyl) as the calibration reference.

Results and Discussion

A typical experiment was conducted with either a 10 μm thick free-standing polyaniline cast film or a 100 nm polyaniline thin film grown on either an ITO (indium−tin oxide) glass electrode or a Pt electrode. All the thin films were grown on the electrodes having the same surface area under the same conditions (e.g., using a constant current density of 13.3×10^{-6} A/cm^2, for 25 min). A series of such prepared polyaniline-coated ITO electrodes were pretreated, by subjecting individual film to an electrochemical forcing in a 0.5 M H_2SO_4 electrolyte solution at different given voltage, such as −0.2, −0.1, 0.1, 0.3, or 0.5 V (vs SCE) for 10 min, before they were all converted to the same oxidation state, e.g., by forcing them to 0.3 V for 10 min. The resultant polyaniline films were then studied with UV−vis−NIR spectroscopy. The results, as summarized in Figure 1, indicated that all, except the sample with −0.2 V pretreatment, the polyaniline-coated electrodes gave similar electronic absorption spectra with the spectroscopic feature for a typical localized polaron (with absorption maximum at 835 nm). But the sample with pretreatment at −0.2 V revealed a broad free carrier tail, similar to that for a polyaniline with delocalized polaron band structure.[13a] A further study showed that the electronic transition as indicated by the change in UV−vis−NIR spectrum of the film pretreated at −0.2 V actually happened gradually within the 10 min treatment period (Figure 2). Figure 2 indicated that such change occurred rather rapidly within about 2.5 min.

Furthermore, such electronic transition from a localized to a more delocalized band structure was also accompanied by a conductivity enhancement effect. For example, the conductivity of a 10 μm thick free-standing polyaniline film (at 0.3 V oxidation state, doped with $HClO_4$) increased rapidly from 1.7 to 12.6 S/cm within 5 min of pretreatment at −0.2 V and then level off at ca. 14.3 S/cm after 60 min (Figure 3), whereas films cast from the same solution and pretreated at −0.1 V for 60 min showed only little improvement on conductivity (2.9 S/cm). Although much higher conductivity (ca. 200 S/cm) have been reported for the polyaniline films cast directly from solution (prepared by a delicate mixing and dissolution process) that contained a functional dopant (camphorsulfonic acid)[13d] as well as a suitable and effective secondary dopant (*m*-cresol),[13a] the best conductivity reported for a preformed polyaniline free-standing film, such as the film cast from its NMP solution, has been consistently to be 1−5 S/cm (after being redoped with HCl or any other protonic acids).[11] Similar results have been obtained with the electrochemically prepared polyaniline films, which also showed a regular bulk conductivity of less than ca. 5 S/cm, even if a good primary dopant (i.e., camphorsulfonic acid) was used for the electrolyte solution. MacDiarmid, Epstein, and co-workers have demonstrated that the surface resistance of a preformed thin polyaniline coating (estimated to be ca. 100−200 nm thick by the reported UV−vis−NIR absorbance) can be reduced via the treatment with the vapor of a good secondary dopant (i.e., *m*-cresol); however, no related results about preformed thick films (e.g., 10 μm thick) were disclosed or discussed.[13c] In the same report, the surface resistance of a thin polyaniline coating (spun from its chloroform solution containing a primary dopants of camphorsulfonic acid) was reduced by 100-fold, from ca. 200 kΩ/square to ca. 2 kΩ/square, after extended exposure (i.e., 2−17 h) to the vapor of a good secondary dopant (i.e., *m*-cresol). In another study by the same workers,[13c] the bulk conductivity of the camphorsulfonic acid-doped polyaniline free-standing film as cast from its chloroform solution was reported to be ca. 0.1 S/cm. On the basis of the above results for the thin film, it is reasonable to assume that the change in bulk conductivity of the polyaniline matrix in preformed thick films should also increased by ca. 100-fold, i.e., from 0.1 to ca. 10 S/cm, if similar posttreatment was adapted.

Furthermore, it was also mentioned[13c] that when polyaniline film was cast from a solution consisting of *m*-cresol (used as the solvent and the secondary dopant) and a typical inorganic acid (as the primary dopant), the conductivity only reached 40 S/cm (with H_2SO_4 dopant) or 26 S/cm (with HCl).[13a] Much lower conductivity would be expected if the secondary dopant was absent (or being removed) from such films. In fact, this conductivity reduction phenomenon has been demonstrated in the same report for camphorsulfonic acid-doped and methanesulfonic acid-doped polyaniline films when the secondary dopant was removed. For example, after all the entrapped *m*-cresol was removed by heating at 195 °C under Ar for 15 min, the conductivity of the corresponding polyaniline reduced from ca. 150 to 80 S/cm for the camphorsulfonic acid-doped film and from ca. 120 to 20 S/cm for the methanesulfonic acid-doped film.

In light of the fact that our −0.2 V treated polyaniline film was doped with an inorganic dopant $HClO_4$ (instead of camphorsulfonic acid) and contained no secondary dopant, its high conductivity of 12.6−14.3 S/cm is worth noting. Apparently much higher conductivity can also be expected from the electrochemical treatment, when the optimal treatment condition is further identified, or if a right combination of functional primary dopant (e.g., camphorsulfonic acid) and secondary dopant (e.g., *m*-cresol) is also concurrently employed under the appropriate conditions and/or processes. The related studies are currently in progress.

It was also found that such a conductivity enhancement effect induced by electrochemical pretreatment was neither caused by difference in dopant distribution pattern (because all $HClO_4$-doped films had even distribution of Cl atom throughout the film thickness, as observed by the depth profiling using SIMS) nor due to any fundamental composition change of the films, as all films had the same doping level (i.e., 52 ± 2%, measured by the atomic ratio of Cl/N using X-ray photoelectron spectroscopy), and their corresponding undoped forms also showed similar IR spectra.

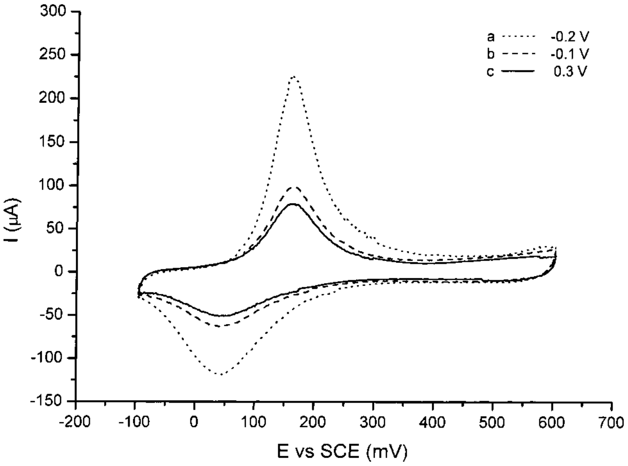

Figure 4. Cyclic voltammogram (CV) in 0.5 M H_2SO_4 for the polyaniline films after a 60 min electrochemical pretreatment (in 0.5 M H_2SO_4) at (a) −0.2, (b) −0.1, and (c) 0.3 V. (The scan range was from −0.1 to 0.6 V at a scan rate of 30 mV/s.) All samples were grown on a 0.5 × 0.5 cm Pt electrode under a constant current density of 13.3×10^{-6} A/cm^2 for 25 min, in a 0.5 M H_2SO_4 aqueous solution that contained 0.1 M aniline.

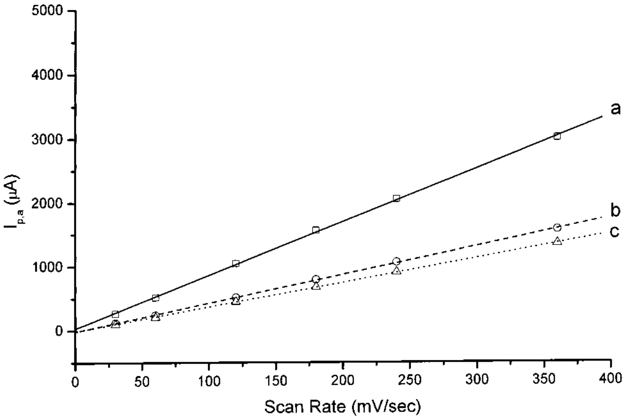

Figure 5. Change in the anodic peak current ($I_{p,a}$) at 0.168 V (vs SCE) against the CV scan rate between −0.1 and 0.6 V in 0.5 M H_2SO_4, for the polyaniline films that have been pretreated with electrochemical forcing in 0.5 M H_2SO_4 for 10 min at a voltage of (a) −0.2, (b) −0.1, and (c) 0.3 V.

The cyclic voltammograms (CV) of both the original and the treated polyaniline films, as displayed in Figure 4, showed similar one pair CV response with same average redox peak potentials (0.099 V) for all samples between −0.1 and 0.6 V (vs SCE). However, the redox peak current of the −0.2 V treated film had increased sharply. The result implied that the −0.2 V treated film has, somehow, a much higher redox rate than the original and other treated films. Further investigations indicated that a linear relationship exists between the anodic peak current and the CV scan rate, as displayed in Figure 5. Such results are consistent with the adsorption model for the electroactive species.[15] Hence, the peak current i_p is linearly proportional to the scan rate ν, the square root of charge diffusion coefficient D, and the concentration of polyaniline C_{ox} according to eq 1,[15]

$$i_p = 0.4463nFA[nF/RT]^{1/2}C_{ox}D^{1/2}\nu \qquad (1)$$

Since all the polyaniline films were prepared under exactly same conditions, it is reasonable to assume that the electrode areas, the concentrations of electroactive species (i.e., polyaniline), and the number of transferred electrons associated with the first anodic peak were, within experimental errors, the same for all series of experiments. Therefore, the relative charge diffusion coefficient between two different voltage-treated polyaniline films can be derived from their slope ratio of peak current I_p vs scan rate ν curves according to eq 2.

$$D_1/D_2 = [(i_{p1}/i_{p2})(\nu_2/\nu_1)]^2 \qquad (2)$$

The charge diffusion coefficient for the −0.2 V (10 min) treated film was found to be about 3.5 and 4.8 times greater than that of the −0.1 and 0.3 V treated

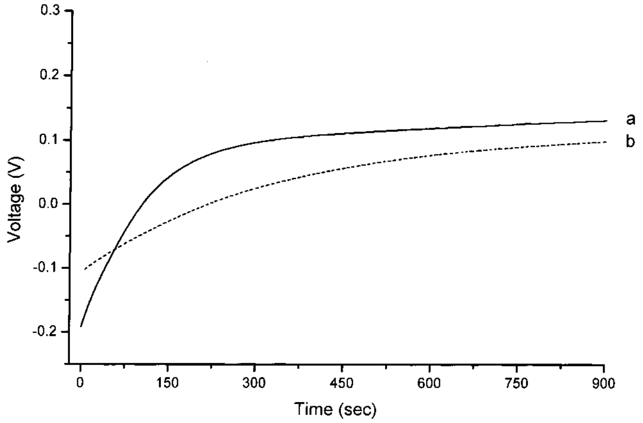

Figure 6. Open-circuit potential vs time for the polyaniline films after being electrochemically treated at (a) −0.2 and (b) −0.1 V.

film, respectively.[15] Furthermore, the −0.2 V treated film was also found to be relatively easier to undergo air oxidation than the −0.1 V treated film. This behavior in ease of oxidation was investigated by monitoring the rate of change on the open-circuit (OC) potential of the corresponding polyaniline film, right after electrochemical forcing treatment, as displayed in Figure 6. The results in Figure 6 showed very clearly that the OC potential of the −0.2 V treated film not only increased at a much faster rate than that of the −0.1 V treated film but also reached a much higher final oxidation potential. All these results suggested that the treatment at −0.2 V seem to induce the formation of a more efficient matrix for charge transport.

The ESR (electron spin resonance) measurements for the doped polyaniline films all showed a typical symmetric ESR signal, except that the peak-to-peak line width (ΔH_{pp}) of the ESR signal for the −0.2 V treated polyaniline film (ca. 0.8 G) was much narrower than that of the original film (ca. 1.3 G). Since both films had the same doping level, the results suggests that the polaronic charge carriers in the −0.2 V treated polyaniline film are more delocalized than those in the original film.[16]

Furthermore, the limiting potential for carrying out the previously mentioned UV−vis−NIR spectral transition was found to be dependent on the type of electrolyte solution employed during the electrochemical pretreatment. For example, if a similarly prepared polyaniline thin film (on ITO) was electrochemically pretreated in an CH_3CN solution containing 0.5 M $LiClO_4$ and 0.1 M $HClO_4$ as electrolyte (followed by reoxidation at 0.3 V in 0.5 M H_2SO_4, before taking the UV−vis−NIR spectra), the limiting potential for carrying out such spectral transition (Figure 7) was found to be as high as ca. 0.1 V (vs SCE), instead of the −0.2 V as observed for the films pretreated in 0.5 M H_2SO_4 aqueous solution. The results in Figure 7 showed that the UV−vis−NIR spectrum for the 0.3 V treated polyaniline film in such CH_3CN electrolyte solution displayed typical spectral features for localized charge carriers, and the spectrum for the 0.1 V treated film showed typical features for delocalized charge carriers, whereas the 0.2 V treated film showed a spectral feature containing both localized and delocalized forms. These results can be rationalized with the change of the CV features (and the redox behaviors as well) of polyaniline in different electrolyte solutions, as illustrated by the CV curves in Figure 8. The results in Figure 8 showed that the first pair of redox peaks of polyaniline in 0.5 M H_2SO_4 aqueous solution was located at 168 mV (for the anodic cycle) and 30 mV (for the cathodic cycle). When the same polyaniline was placed in the above-mentioned CH_3CN electrolyte solution, the first pair of redox peaks of polyaniline was shifted to 255 mV (for the anodic cycle) and 191 mV (for the cathodic cycle), indicating that polyaniline can be fully reduced to leucoemeraldine form at relatively higher potential in CH_3CN solution. Furthermore, when compared with the redox peak of polyaniline in 0.5 M H_2SO_4 electrolyte solution, the redox activity of the first anodic peak of polyaniline in CH_3CN electrolyte solution appeared to happen within a much narrower voltage range. In addition, while the redox current for the CH_3CN system reduced quickly to zero at between 0.1 and 0.2 V, the corresponding redox current for the H_2SO_4 system showed gradual reduction and reached zero at a much lower voltage.

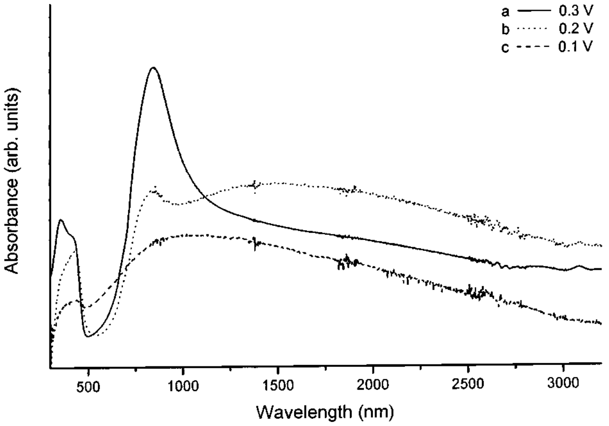

Figure 7. UV−vis−NIR spectra for the polyaniline films measured at an oxidation state of 0.3 V (vs SCE) in 0.5 M H_2SO_4 aqueous solution, after a 10 min electrochemical pretreatment (in CH_3CN containing 0.5 M $LiClO_4$ and 0.1 M $HClO_4$) at (a) 0.3, (b) 0.2, and (c) 0.1 V.

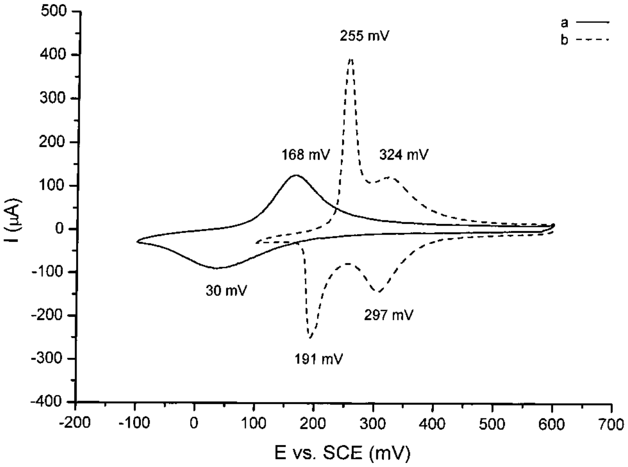

Figure 8. Cyclic voltammogram (CV) of as prepared polyanilines scanned at a rate of 30 mV/s between −0.1 and 0.6 V (vs SCE) in (a) 0.5 M H_2SO_4 aqueous solution and (b) CH_3CN solution containing 0.5 M $LiClO_4$ and 0.1 M $HClO_4$.

In light of all the above results, we believed, as the film was treated at −0.2 V (in 0.5 M H_2SO_4 aqueous solution), the polyaniline backbone was gradually converted from the emeraldine form to the fully reduced leucoemeraldine form within the 10 min treatment duration. Furthermore, it is also believed that, accompanied by this reduction treatment, the overall strength of interchain H-bonding interactions that existed between the diiminoquinoid and the diaminobenzoid repeat units[17] also gradually diminished with the decrease in the total number of diiminoquinoid repeat units. Such reduction in interchain interactions should lead to higher local chain motion freedom and encourage a conformational change from a relatively compact coil to a more expanded coil structure (similar to what happened when polyaniline was treated with a "secondary dopant"[13]), thus creating a more effective conjugated network or matrix. Furthermore, when the polyaniline is in an oxidation state other than the leucoemeraldine form, i.e., at an oxidation voltage equal to or greater than about −0.1 V (vs SCE in 0.5 M H_2SO_4), it may still contain a significant amount of diiminoquinoid unit whose extent of interchain H-bonding can still effectively prevent the above-mentioned chain conformational change.

The results in this report may also provide additional valuable insights for understanding how a secondary dopant may actually help to promote the conformational change of polyaniline backbones in a solid matrix.

Conclusion

A new electrochemical method for enhancing the conductivity of a preformed polyaniline film has been established. This new method is environmental friendly and fast. It works well in an aqueous solution without the need of using toxic organic solvent, e.g., *m*-cresol as a secondary dopant. For a 100 nm thick polyaniline film, the treatment time can be less than 2.5 min. Furthermore, this method is also applicable for a preformed thick polyaniline film, e.g., 10 μm thick. By simply forcing the polyaniline film at an effective electrochemical voltage capable of transforming the polyaniline to its fully reduced form, the conductivity of such polyaniline film can be easily enhanced by an order of magnitude within a pretreatment time as short as ca. 5 min. The discovery of this novel electrochemical method opens up a new dimension for controlling and/or enhancing the conductivity of polyaniline, which are critical for many practical applications of conducting polymers.

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