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Palladized aluminum as a novel substrate for electrosynthesis of polyaniline in sulfuric acid solutions

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Abstract The electropolymerization of aniline on a palladized aluminum electrode (Pd/Al) by potentiodynamic as well as potentiostatic methods is described. The effect of the monomer concentration between 0.01 and 0.4 M on the polyaniline (PANI) formation and its growth on the Pd/Al electrode was investigated and a suitable concentration of 0.2 M is suggested. A similar study was carried out to investigate the effect of sulfuric acid concentration and 0.1 M sulfuric acid was chosen. A study on the influence of electropalladization time on the polymer formation and its growth suggested a convenient time of 40 s. The stability of the PANI film on the Pd/Al electrode was studied as function of the potential imposed on the electrode. For applied electrode potentials of 0.1–0.7 V, the first-order degradation rate constant, k, of PANI film varies between 1×10^{-6} and 2×10^{-5} s^{-1}, and a relatively low slope (i.e., 2.2) was obtained for the plot of log k versus E. The coatings were characterized by scanning electron microscopy (SEM), and cyclic voltammetric behavior of the PANI-deposited Pd/Al electrode is discussed. The electrocatalytic activity of the PANI-deposited Pd/Al electrode against $para$-benzoquinone/hydroquinone (Q/H$_2$Q) and Fe(CN)$_6^{3-}$/Fe(CN)$_6^{4-}$ redox systems were investigated and on the basis of $\Delta E_p = E_p^a - E_p^c$ of the corresponding cyclic voltammograms and the redox systems were identified as the reversible and quasi-reversible systems, respectively.

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Introduction

Conducting polymers, such as polyaniline (PANI), are easily electrosynthesized at inert electrodes (e.g., platinum, gold, and carbon) [1–11], but electrosynthesis of these polymers is more difficult at reactive electrodes such as aluminum. This is connected to a thin, but highly stable protective oxide, Al$_2$O$_3$, which is normally present on aluminum surface or may be formed under anodic conditions and alters the kinetics of electron-transfer reactions during electropolymerization. Despite these problems, electropolymerization on inexpensive and more available substrates such as Al, is more interesting than on expensive substrates in view of commercial applications. Chemical or electrochemical pre-treatment of the aluminum surface to prevent the formation of Al$_2$O$_3$ as well as to lower the electrooxidation potential of aniline seems to be a suitable approach to electrodeposition of stable and adherent PANI films on the aluminum electrode. There have been much fewer reports on the direct preparation of polyaniline on aluminum electrode. For example, Conroy et al. [12] reported the electrodeposition of PANI at pure aluminum from tosylic acid solution containing aniline. Abalyaeva et al. [13] used transition metal ions as catalysts for the electrodeposition of PANI on an Al electrode. Motheo et al. [14] used anodic activated aluminum in nitric acid solution containing aniline for electrosynthesis of PANI on the aluminum surface. Recently Huerta-Vilca et al. [15] used

alizarin as a chelating agent for decreasing the working electrode potential in the synthesis of PANI on an Al electrode under a galvanostatic regime.

In previous work we have shown that deposited metallic palladium on the Al substrate catalyzes the oxidation of some organic and inorganic materials such as oxalic acid, ascorbic acid, paracetamol, and nitrite [16, 17]. The palladium-coated aluminum electrode also shows good behavior for immobilization of some inorganic polymers such as Prussian blue and its analogs [18]. To the best of our knowledge, there is no report devoted to the electro-synthesis of PANI on bulk Pd or Pd-coated surfaces. In the present work we have adapted a simple procedure for protection of the aluminum surface by dipping it in $Pd(NH_3)_4^{2+}$ solution [19] and used the palladium-coated aluminum electrode (Pd/Al) as a novel matrix for the electropolymerization of aniline. We also intended to study the electrochemical and electrocatalytic properties as well as the stability of the PANI-deposited Pd/Al electrodes. Finally the influence of some experimental factors on the polymer growth at the electrode was studied.

Experimental

Chemicals and reagents

An aluminum bar with certified purity of 99.9% (purchased from Tabriz Wire & Cable MFG. CO, Simcat, Iran) was used as substrate. $PdCl_2$, H_2SO_4, aniline, H_2Q, $K_4Fe(CN)_6$, $K_3Fe(CN)_6$, and other chemicals were of analytical grade and purchased from Merck. Aniline was purified by distillation and stored in the absence of light.

Instrumentation

Electrochemical experiments were carried out using an AUTOLAB PGSTAT-30 potentiostat/galvanostat connected to a personal computer through a USB electrochemical interface. A conventional three-electrode cell was used. The working electrode was a Pd/Al (with a diameter of 3 mm); a saturated calomel electrode (SCE) and a platinum wire were used as the reference and auxiliary electrodes, respectively. Scanning electron microscopy (SEM) was performed on a LEO 440i Oxford instrument.

Procedures

Preparation of working electrode

A cylindrical aluminum bar of 90-m length and 12-mm diameter was used for preparation of the disk aluminum electrode as follows: one end of the bar was threaded by means of a suitable screw tap in order to connect it to an available holder or rotating disk system. From other end of the bar, one part (30 mm in length) was ground to a diameter of 3 mm and was then fitted into a prefabricated hole in a Teflon rod of 30-mm length and 12-mm diameter [20]. The aluminum surface fitted in the Teflon was mechanically polished successively to a mirror finish, first with 200, 600, 1,000, and 1,500 emery papers and then with 0.05-μm alumina powder. The polished surface was cleaned by dipping in concentrated HCl for about 1 min and then rinsed with doubly distilled water.

The freshly polished Al electrode was coated with metallic Pd by dipping it in 50 mM $Pd(NH_3)_4Cl_2$ for 40 s to obtain a Pd coating of about 0.03 mg cm^{-2}. The palladized aluminum electrode (Pd/Al) was rinsed with doubly distilled water and then used as the working electrode for electropolymerization of aniline.

Evaluation of deposited Pd on the Al electrode

The amount of Pd (mg cm^{-2}) deposited on the Al electrode was evaluated from the charge consumed for total anodic stripping of metallic Pd from the Al surface at a controlled potential of 0.7 V vs. SCE in the presence of an excess amount of Cl$^-$ ion (50 mM) to form $PdCl_4^{2-}$ according to the following reaction:

$$Pd(Al) + 4Cl^- \rightleftharpoons PdCl_4^{2-} + 2e^- \qquad (1)$$
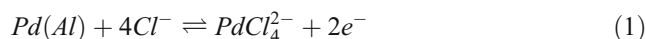
Electropolymerization of aniline

Electropolymerization of aniline on the Pd/Al electrode was performed by a potentiodynamic method at a scan rate of 50 mV s^{-1} between −0.2 and 1.0 V or a potentiostatic method at 0.8 V versus SCE in 0.1 M H_2SO_4 as electrolyte solution containing 10–400 mM aniline. For the purpose of electrochemical characterization, the PANI was grown for 10 or 24 cycles, and the electrodes were washed thoroughly in 0.1 M H_2SO_4 prior to their use.

Stability of PANI-modified electrodes

The experiments on the electrochemical stability of the PANI-modified electrodes were performed by holding the electrode in a supporting electrolyte, containing 0.1 M H_2SO_4, under a controlled potential, ranging from 0.1 to 0.7 V. At definite time periods, cyclic voltammograms of the electrode were recorded within the potentials limits of −0.2 to 1.0 V, and the anodic peak current obtained was used in calculations.

Fig. 1 *Left* cyclic voltammograms (24 cycles) recorded during potentiodynamic growth of PANI film on the Pd/Al electrode in solution containing 0.2 M aniline and 0.1 M H_2SO_4 at a scan rate of 50 mV s^{-1}. *Right* plot of total anodic charge as a function of cycle number during potentiodynamic growth of PANI on the Pd /Al electrode (*1*), on the Pt electrode (*2*), and on the bare Al electrode (*3*) (in this case the concentration of aniline is 0.4 M)
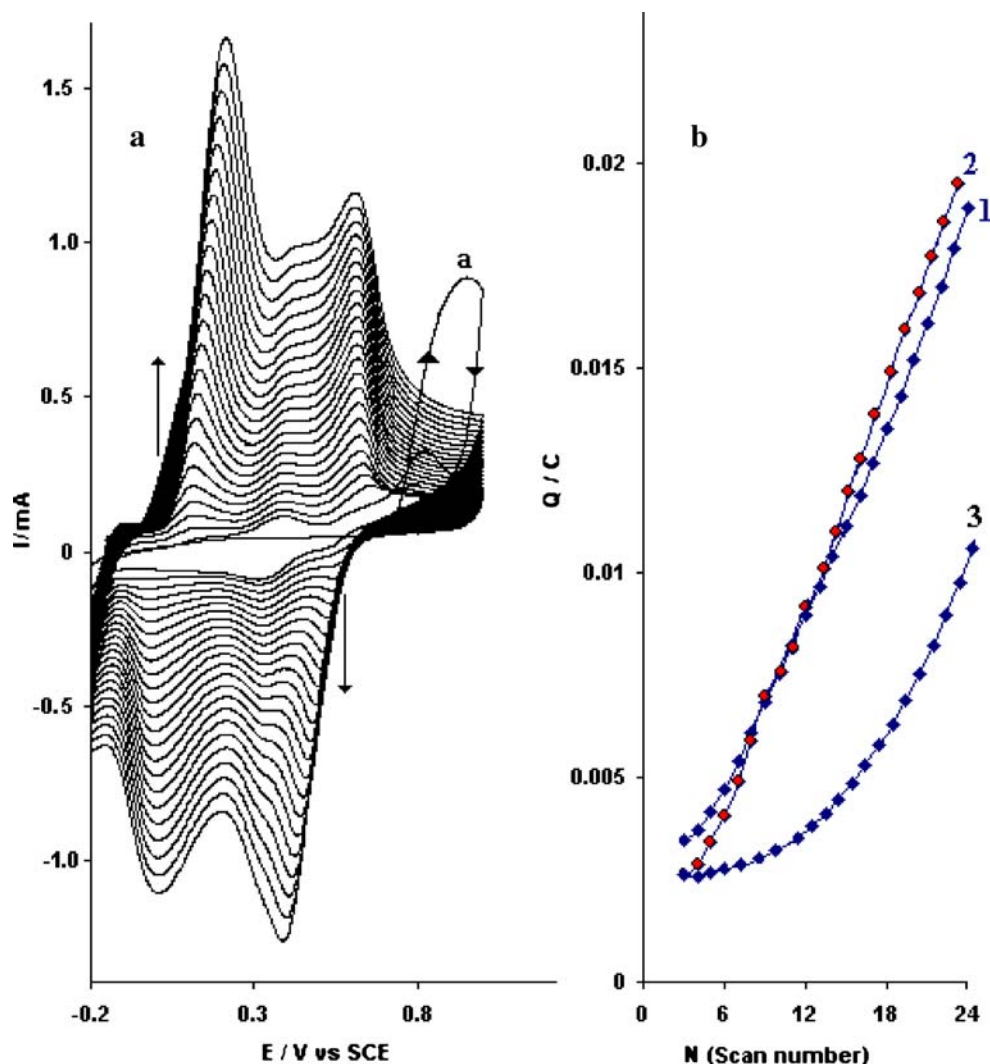
SEM characterization of PANI

The morphology of the PANI on the Pd/Al electrode was investigated with a scanning electron microscope operated at 10.0 kV. SEM specimens were prepared by electrosynthesis of PANI on the electrode substrates and the electrodes were then cut at about 2 mm and mounted. A small amount of Au was vaporized onto the surface of the PANI samples to allow clear micrographs to be obtained.

Electrocatalytic properties of PANI-modified electrodes

For studies of redox reactions, standard solutions of H_2Q, $K_4Fe(CN)_6$, and $K_3Fe(CN)_6$ were prepared and diluted to the required concentration in 0.1 M H_2SO_4. Equal concentrations of $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$ were used in each electrolyte. H_2Q alone was used for the Q/H_2Q reaction.

Results and discussion

Formation and growth of PANI

The electrooxidation of aniline leading to polymerization follows a two-electron transfer process [21]. Although many electrochemical techniques are suitable for nucleation and growth of PANI, in the present work, potentiodynamic and potentiostatic procedures are used. Our preliminary investigation showed that the deposition of PANI on the bulk Pd electrode does not take place even for aniline solutions of high concentrations due to the oxidation of aniline which may occur at a potential more positive than the oxidation of the electrode. Cyclic voltammetry of aniline on the Pd/Al electrode showed that the aniline was easily oxidized at the electrode surface. The behavior of the Pd/Al electrode in the aniline oxidation may be attributed to the morphologic aspect and physical status of Pd coating
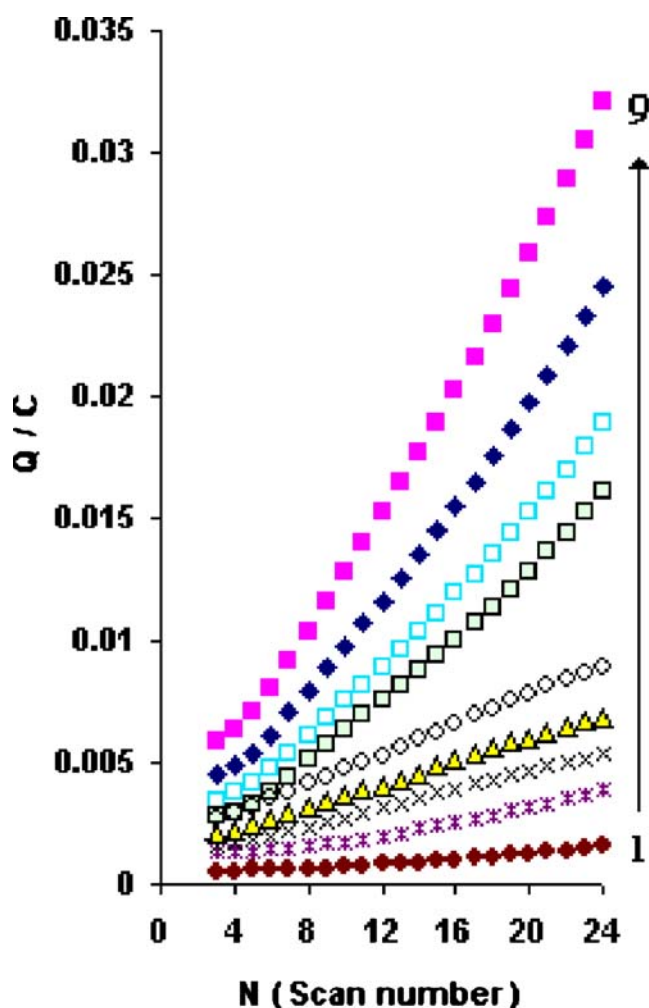
Fig. 2 Plot of total anodic charge as a function of cycle number during potentiodynamic growth of PANI on the Pd /Al electrode from *1* 0.01, *2* 0.02, *3* 0.03, *4* 0.04, *5* 0.05, *6* 0.1, *7* 0.2, *8* 0.3, and *9* 0.4 M aniline in 0.1 M H₂SO₄ at a scan rate of 50 mV s⁻¹

because it is known that the physical and chemical properties of a thin metal layer on foreign substrates are different from the bulk metal [22–24]. Cyclic voltammograms of PANI deposition from 0.2 M aniline in 0.1 M H₂SO₄ solution in the potential range between −0.2 and 1.0 V at a scan rate of 50 mV s⁻¹ are shown in Fig. 1. In the first potential sweep, the oxidation of aniline occurs at about 0.95 V (peak a) as a distinct irreversible broad anodic peak. In the first reverse cycle, new cathodic peaks appear, which are almost reversible, confirming the initial deposition of electrooxidized products. During the subsequent scan, the oxidation of aniline which favors the adsorption of aniline and deposition of PANI, occurs at about 0.85 V due to the catalytic effect of PANI, which results in a growth of the deposit. The anodic peak at 0.14 V is attributed to the transformation of PANI from the reduced leucoemaraldine (LE) state to the partly oxidized emeraldine (EM) state [21]. The anodic peak at 0.62 V corresponds to transition of the

PANI from (LE) to pernigraniline (PE) state, and an anodic hump at 0.5 V, which is generally attributed to redox reaction of *p*-benzoquinone, also appeared. Reaction intermediates such as *p*-benzoquinone, *p*-aminophenol, and some dimers are known to become trapped in the polymer during the polymerization [21]. The variation in the peak potentials with scan number is not substantial. In electro-polymerization processes the increase of the voltammetric peak current or charge in cyclic voltammograms with sweep number is an indication for polymer growth. The results for the total charge under anodic peaks from the CV deposition of PANI on Pd/Al and Pt versus scan number are also shown in Fig. 1. As seen in Fig. 1b, the nature of the growth rate on the Pd/Al (curve 1) is comparable to that observed on Pt (curve 2) but quite different from that observed on the bare Al [15].

The electrooxidation of aniline on bare Al is possible from an aniline solution with concentration higher than 0.35 M, but the polymer growth is very slow (curve 3) and PANI film on the electrode is less adherent and less stable (results are not shown). Therefore, when the film was rinsed with water the PANI film peeled off easily from the electrode.

Effect of monomer and sulfuric acid concentrations

The influence of the monomer concentration on the growth of the PANI film on the Pd/Al electrode was investigated by cyclic voltammetry. By measuring the total charge of anodic peaks of the monitored CVs, Q_a, the film growths were evaluated and are shown in Fig. 2. The film begins to grow at very low concentrations of aniline, and the growth rate increases with monomer concentration. These results indicated that the induction time for deposition of PANI even in a very low concentration of aniline is negligible compared to that observed on bare aluminum which is infinite in the range of 0.01–0.3 M aniline [15]. The effect of sulfuric acid concentration on the deposition of PANI was also studied and the total anodic charge against scan number during PANI deposition from H₂SO₄ solution with a concentration of 0.01–0.3 M is shown in Fig. 3. The PANI film thickness for a given cycle number and growth rate increased with increasing H₂SO₄ concentration. Similar behavior was reported in the literature for PANI growth on Pt, Ni, Ti, and stainless steel [24]. Note that the adherence of the PANI film decreases with concentration of H₂SO₄. On the other hand the anodic middle current peak (0.5 V) increases in magnitude with concentration of H₂SO₄, thus suggesting the presence of increasing concentrations of reaction intermediate products. However in order to prevent the detachment of PANI film from the electrode surfaces and formation of reaction

intermediate product, a moderate H_2SO_4 concentration of 0.1 M was used in the present work.

Effect of palladization time

The effect of palladium coating time on cyclic voltammograms of PANI deposited from 0.20 M aniline in 0.1 M H_2SO_4 was investigated. The total deposition consisted of 24 cycles with the last cycle being subjected to characterization. The cyclic voltammograms of the 24th cycle showed that the peak potential of the PANI characterization peaks remained almost unchanged, while the corresponding currents increased with coating time between 0 and 40 s and leveled off at 40 s (Fig. 4a). Figure 4b displays also the PANI growth on the Pd/Al for different dipping times of Al in $Pd(NH_3)_4^{2+}$ solutions. As seen in Fig. 4b the growth rate of PANI is dependent on the dipping time between 0 and 40 s and becomes nearly independent after 40 s. Indeed the induction time for short palladium coating times is long, compared with those observed for long coating times. Therefore an optimum coating time of 40 s is suggested.
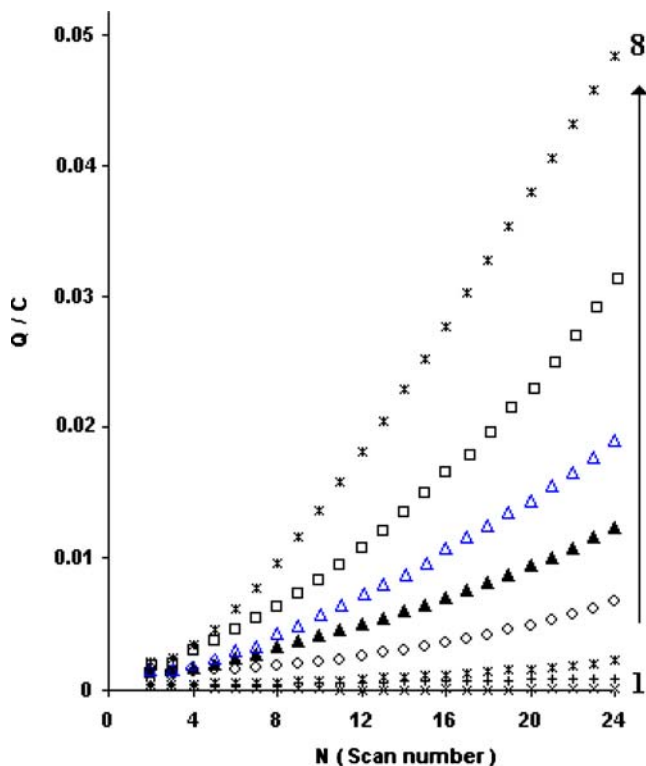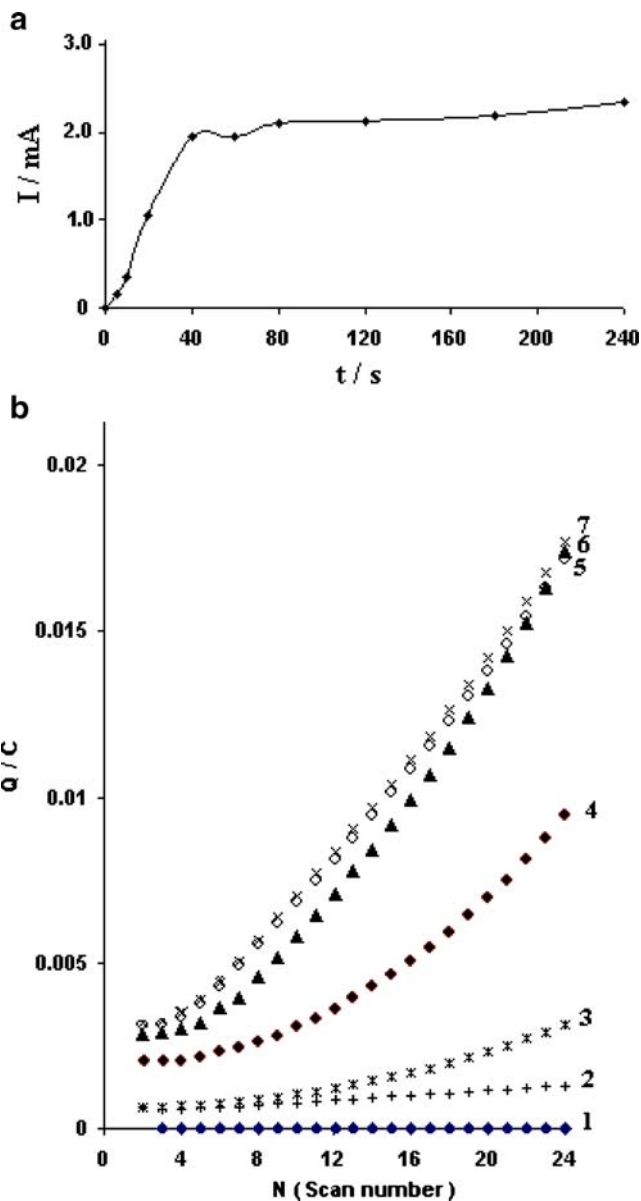
Fig. 4 **a** Plot of cyclic voltammogram peak current (peak LE/ME) for the 24th cycle of potentiodynamic growth of the PANI film on the Pd/Al electrode in a solution containing 0.2 M aniline and 0.1 M H_2SO_4 at a scan rate of 50 mV s^{-1} versus palladization time of aluminum electrode in 5×10^{-3} M $Pd(NH_3)_4^{2+}$ solution. **b** Plot of total anodic charge as a function of cycle number for PANI deposition from 0.2 M aniline in 0.1 M H_2SO_4 at a scan rate of 50 mV s^{-1} versus palladization time of aluminum electrode in $5 \times 10^{-3} Pd(NH_3)_4^{2+}$ solution: *1* 0, *2* 5, *3* 10, *4* 20, *5* 40, *6* 60, and *7* 80 s

Characterization of PANI-deposited Pd/Al electrodes

Electrochemical characterization

Cyclic voltammetric behavior of the PANI deposited on the Pd/Al electrode is characterized by three pairs of current peak in 0.1 M H_2SO_4 solution in the absence of the monomer (Fig. 5). These peaks are due to doping and undoping of proton and anions with PANI molecules. The

Fig. 3 Plot of total anodic charge for PANI deposition from 0.2 M aniline in *1* 0.01, *2* 0.02, *3* 0.03, *4* 0.05, *5* 0.07, *6* 0.1, *7* 0.2, and *8* 0.3 M H_2SO_4 at a scan rate of 50 mV s^{-1} as a function of cycle number on the Pd/Al electrode

Fig. 5 Cyclic voltammograms of PANI-deposited Pd/Al electrode in 0.1 M H_2SO_4 at the scan rate of *1* 10, *2* 25, *3* 50, *4* 75, and *5* 100 mV s^{-1}. *Inset*I_{pa} (LE/EM) as a function of scan rate for PANI /Pd/Al
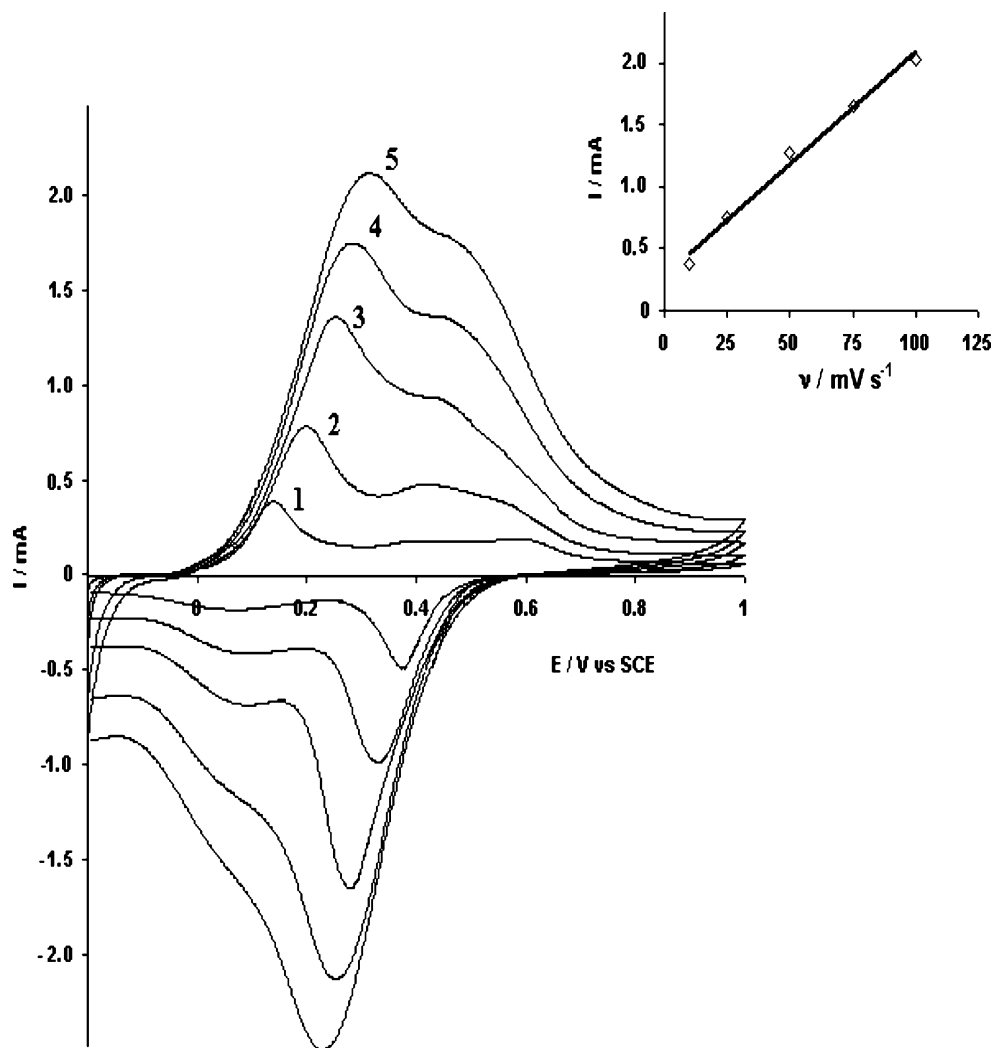
current peak around 0.2 V is attributed to LE/EM transformation of PANI; current peak around 0.6 V is due to EM/PE transformation; the peak at 0.5 V was not resolved well. As seen in the inset in Fig. 5, the magnitude of current increase linearly with scan rate *v* for PANI on the electrode, thereby indicating the surface redox characters. However the LE/EM and EM/PE peaks shift with scan rates and became broad, and the cathodic LE/EM redox peak is not clearly observed in all cases.

SEM characterization

Figure 6 shows typical SEM images of PANI grown on the Pd/Al electrode in H_2SO_4 solution by using the potentiodynamic and the potentiostatic methods. As can be see in Fig. 6a,b, the PANI film has a compact structure with larger grain shapes; as the number of cycles increases, the size of the grains increases and the surface of the electrode is coated completely with PANI grains. On the other hand, in the beginning of polymerization process, the growth of polymer is in two dimensions; after the complete coating of

the electrode surface the growth of PANI continues perfectly in three dimensions.

The PANI films obtained from potentiodynamic and potentiostatic methods have almost the same morphology; however, the potentiodynamic method produced larger grain sizes and PANI films with a more compact structure than the potentiostatic method. Similar behavior for PANI growth was reported previously [21, 25].

Stability study

For many applications, the stability of the PANI-deposited electrode is of great importance. It is well known that PANI undergoes electrochemical degradation by application of sufficiently high anodic potentials [26]. The current peaks in cyclic voltammograms of PANI diminish in height during prolonged potential cycling. Also, by holding the PANI-modified electrode for some time at a controlled potential in a supporting electrolyte, some changes in cyclic voltammograms are observed (e.g., both anodic and
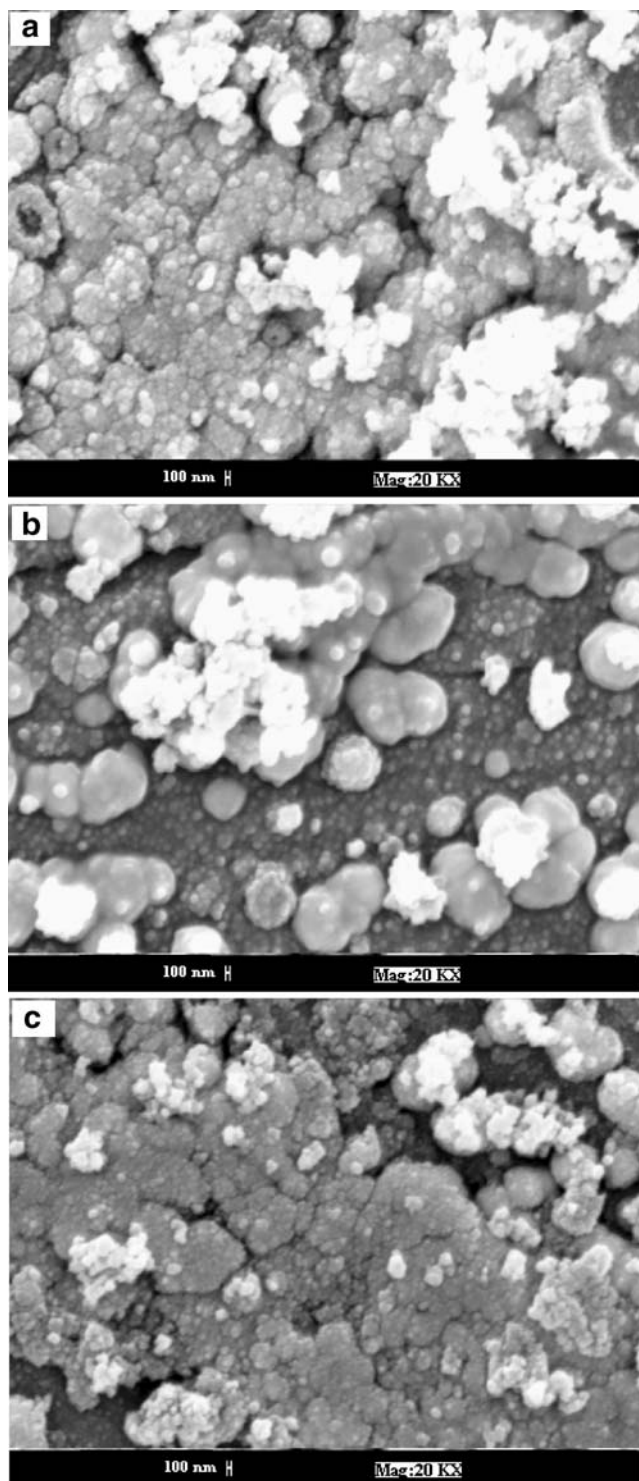
Fig. 6 SEM images of PANI deposited on Pd/Al electrode by potentiodynamic method from 0.2 M aniline in 0.1 H_2SO_4 after 24 cycles (**a**), 10 cycles (**b**), and by potentiostatic method (**c**)

cathodic parts of the two characteristic redox transitions diminish in height). The only reason for this is the degradation or decomposition of the PANI film, leading to low molecular weight decomposition products [27–29]. The

degradation products are usually identified as *p*-benzoquinone/*p*-hydroquinone and *p*-quinoneimine/*p*-aminophenol redox couples [28], and the rate of this degradation depends on the electrode potential applied. Study of the time dependence of a relative current of anodic peak LE/EM for a PANI-modified electrode held at different potentials for various times showed that the anodic peak current diminishes with time in all applied potentials. However, the rate of PANI degradation depends on the potential applied and is greater for higher potential values [30]. The data obtained for PANI on the Pd/Al electrode can be easily transformed according to a single 2-parameter exponential decay equation [31]:

$$I_{rel} = a\, e^{-bt} \quad \text{or} \quad \log I_{rel} = \log a - (b/2.3)t \qquad (2)$$

where I_{rel} is a relative anodic peak current, t the reaction time, and a and b are the empirical coefficients.

It follows from Eq. (2) that in terms of chemical kinetics, the coefficient b represents the first-order degradation rate constant (k). Thus, k can be easily obtained by treating the kinetic data according to Eq. (2). A typical plot of $\log I_{rel}$ versus t for the electrode potential of 0.7 V vs. SCE is shown in Fig. 7a for PANI deposited on Pd/Al electrode. The values of k obtained from slope of this kind of plots for different potentials held (0.1–0.7 V), ranged between 1×10^{-6} and 2×10^{-5} s^{-1}. On the other hand when $\log k$ was plotted against electrode potential E, a linear dependence was obtained for PANI on the Pd/Al electrode (Fig. 7b).

By fitting these dependencies to the following linear equation:

$$\log k = c + dE \qquad (3)$$

where c and d are the empirical coefficients, we obtain a slope d of 2.2 at potentials 0.1–0.7 V versus SCE. The slope for PANI on the Pd/Al electrode is close to the value of 1.4 reported for PANI on Pt [32], revealing a much lower sensitivity of PANI degradation to an increasing electrode potential from 0.1 to 0.7 V.

Redox reactions on PANI-deposited electrodes

Studies by cyclic voltammetry on H_2Q oxidation and $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ redox reaction suggested an increase of reaction rate in solution by several orders of magnitude compared to the data on Pt [24]. In the present work, the PANI-deposited Pd/Al was used to study the redox reactions and data obtained were compared with those obtained for bare Pd/Al electrode. Cyclic voltammograms of bare and PANI-deposited Pd/Al electrodes in 0.1 M H_2SO_4 consisting of H_2Q are shown in Fig. 8a. Voltammograms of the electrodes

Fig. 7 **a** Typical plot of the relative current I_{rel} of anodic peak for PANI-modified Pd/Al electrode held at 0.7 V. **b** Dependence of logarithm of the first-order degradation rate constant (log$k$) on the electrode potential for PANI-deposited Pd/Al electrode
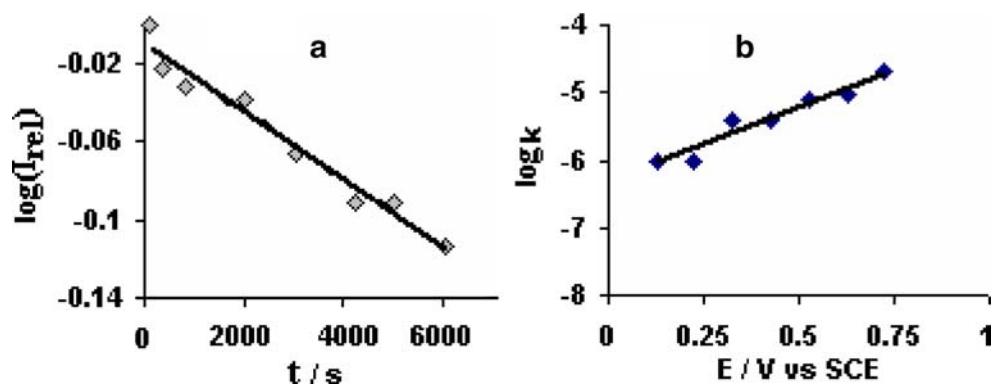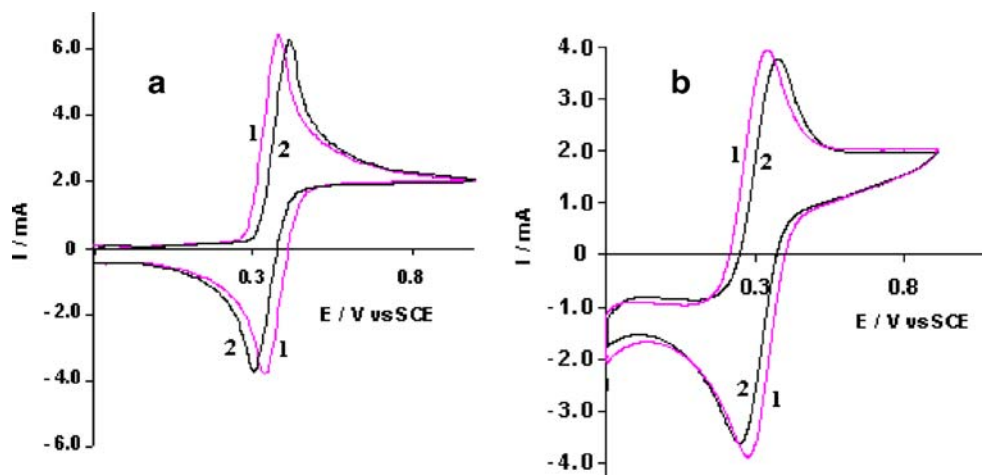

are characterized by a pair of current peaks corresponding to following reaction:

$$Q + 2H^+ + 2e^- \rightleftharpoons H_2Q \qquad (4)$$
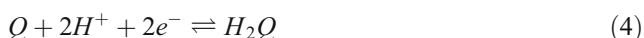
The peak potential separation $\Delta E (\Delta E = E_p^a - E_p^c)$ in the case of PANI-deposited Pd/Al is about 43 mV, which indicates a catalytic effect of PANI in relation to the bare Pd/Al electrode (ΔE is 111 mV). On the other hand, the peak current (i_p) increases with increasing H_2Q concentration, which is expected for a diffusion-controlled electrochemical reaction (data not shown). Similar results were obtained for the $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ redox reaction; typical cyclic voltammograms are shown for bare and PANI-deposited Pd/Al electrodes in Fig. 8b. The potential separation ΔE is about 60 mV, which also indicates a catalytic effect of PANI in relation to the bare Pd/Al electrode (ΔE is 117 mV). Note that the catalytic effect of the PANI-deposited Pd/Al electrode for the Q/H$_2$Q system is comparable to that on the PANI-deposited Pt electrode (ΔE is 45 mV) but higher than that on the PANI-deposited non-platinum metals such as stainless steel, Ni, Al, and Pb [33].

Conclusion

The experimental results reported here demonstrate unambiguously the suitability of the palladized aluminum surface as a novel substrate for the electropolymerization of aniline on the electrode even using a concentrated sulfuric acid solution (i.e., 0.3 M) and relatively diluted monomer solution (i.e., 0.2 M). This new strategy is a straightforward way to prepare a PANI film that is adherant and stable on the Al surface. In the electrode potential region of 0.1–0.7 V, the first-order degradation rate constant, k, of PANI film varies between 1×10^{-6} and 2×10^{-5} s^{-1}. On the other hand the variation of k with potential over the region of 0.1–0.7 V shows a relatively low slope of 2.2, indicating a weak dependence of degradation rate on potential. The PANI-deposited Pd/Al also possesses better electrochemical features and higher electrocatalytic activity than those of PANI film formed on the surface of non-platinum metals [24], but comparable to that on the platinum electrode [33]. Cyclic voltammetric behavior of the PANI deposited on conventional electrodes is generally characterized by three pairs of current peaks in H$_2$SO$_4$ electrolyte [21], which is reproducible in this study for the PANI deposited on the Pd/Al electrode. The proposed strategy is an effective procedure

Fig. 8 Cyclic voltammograms of PANI /Pd/Al (*1*) and bare Pd/Al (*2*) electrodes recorded with scan rate of 10 mV s^{-1} in the potential range between −0.2 and 1.0 V vs. SCE in 0.1 M H$_2$SO$_4$+100 mM H$_2$Q (**a**) and 100 mM Fe(CN)$_6^{3-}$/ Fe(CN)$_6^{4-}$ (**b**)

for the coating of metallic aluminum with PANI even in large-scale practical applications.

This strategy could be utilized for the preparation of inexpensive conductive polymer matrix for dispersion of the platinum group micro particle catalysts which are used as anodic materials in the methanol-based fuel cell. This kind of study is in progress in our laboratory.

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