# ORIGINAL PAPER

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# Copolymers and two-layered composites of poly(*o*-aminophenol) and polyaniline

**Abstract** Electroactive conducting copolymers of aniline (ANI) and *o*-aminophenol (OAP) and two-layered poly(*o*-aminophenol) (POAP)/polyaniline (PANI) composites were prepared in aqueous acidic solution by electrode potential cycling. Copolymerization was carried out at different feed concentrations of OAP and ANI on a gold electrode. A strong inhibition of electropolymerization was found at a high molar fraction of OAP in the feed. The copolymers showed good adherence on the electrode surface and gave a redox response up to pH = 10.0. Two transitions were observed in the in situ conductivities of the copolymers (as with PANI), but the conductivities were lower by 2.5–3 orders of magnitude as compared to PANI. Electrosynthesis of PANI on POAP modified electrodes showed copolymer formation after reaction initiation and finally formation of a PANI layer at the copolymer/solution interface. The 'memory effect' of the bilayer structures of both polymers was discussed in terms of protonation/deprotonation and anion consumption taking place during redox processes of both polymers.

**Keywords** Polyaniline · Poly(*o*-aminophenol) · Copolymerization · Polymer composites

## Introduction

Intrinsically conducting polymers attract significant interest as promising candidates for various applications in e.g. electrocatalysts, electrochromic devices, solar cells and in rechargeable batteries [1–3]. Among conducting polymers polyaniline (PANI) has occupied the prime position because of its high conductivity, good redox reversibility, swift change of color with potential and good environmental stability [4]. Extensive research is

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underway to improve the properties of PANI, either via the polymerization of substituted monomers and post-treatment or copolymerization of aniline (ANI) with other monomers [2, 3].

Polymerization of ring-substituted ANIs [5, 6] or *N*-substituted [7, 8] ANIs have been reported. Yue and Epstein [9] have synthesized self doped PANI through the reaction between an emeraldine base form of PANI and fuming sulfuric acid. The resulting polymer was a soluble type with ring-substituted sulfonic acid group and having a conductivity of about 0.1 S cm$^{-1}$. Increased solubility has been reported for alkyl- and alkoxy-substituted PANIs [10, 11].

Copolymerization of ANI with some of its derivatives, which bear various functional groups, leads to modified copolymers having some remaining functionalities and possessing interesting properties. The primary advantage of copolymerization is the possible homogeneity of the resulting material, the properties of which can be regulated by adjusting the ratio of the concentrations of the monomers in the feed. Karyakin et al. [12, 13] obtained self doped PANI by the copolymerization of ANI with some carboxyl- and sulfonyl-substituted derivatives. Wei et al. [14] reported electrochemical copolymerization of ANI with *o*/*m*-toluidines. Copolymerization of ANI with *o*-aminobenzonitrile yielded copolymers bearing cyano-groups. These copolymers show electrochromic properties different from those of PANI [15]. Accelerations of the rate of electropolymerization of ANI with *p*-phenylenediamine and retardation with *m*-phenylenediamine have been reported [16–18].

Closely related to the electrochemically synthesized copolymers are bilayer systems, formed by the subsequent electropolymerization of two layers of different polymers on the same electrode surface. Several reports are available on systematic investigations and useful applications of such bilayer structures in the field of sensors [19, 20]. Malinauskas et al. [21, 22] reported electrochemical and spectroscopic properties of electrosynthesized copolymers and bilayer structures of PANI

and poly(*o*/*m*-phenylenediamine). In the last few years *o*-aminophenol (OAP), an ANI derivative, has attracted much attention. OAP can be polymerized by suitable oxidation either chemically or electrochemically [23–26]. The electropolymerization of OAP has been investigated with electrochemical techniques [27], ellipsometry [28], in situ Raman spectroscopy [29] and impedance measurements [30]. Poly(*o*-aminophenol) (POAP) has been assigned the structure of a ladder polymer based on repeating phenoxazine units.

A preliminary study of Mu [31] on the copolymerization of ANI (0.2 M) and OAP demonstrated that a small addition of OAP (0.01 M) to the ANI solution could result in copolymer formation on a platinum electrode. However, OAP concentration greater than 0.01 M in the feed strongly inhibited the growth of the copolymer and the author suggested that for higher OAP concentration in the feed the copolymer could not grow. Moreover, the upper potential limit for the homopolymer synthesis was rather high which could result in the overoxidation of ANI and partial degradation of PANI and is also not suitable for POAP synthesis as is shown below with new experimental results and is well known in the literature [25, 32]. Therefore, further information about polymer growth from solutions containing both monomers and properties of the deposited films is needed for practical applications. In the present work we report the results of electrochemical copolymerization of ANI and OAP and bilayer structures of the polymer film derived from these monomers.

## Experimental

All chemicals were of analytical grade. ANI (Riedel-de Häen) was distilled under vacuum and stored under nitrogen in a refrigerator. OAP (Fluka purum) was used as received. 18 MΩ water (Seralpur pro 90C) was used for solution preparation. All solutions were prepared with 0.5 M sulfuric acid (Merck) supporting electrolyte. The influence of pH on the electrochemical activity of homopolymers and copolymers was determined in 0.3 M $Na_2SO_4$ solution. The pH values were determined using an MV81 Präcitronic pH meter with standard buffers.

Thin films of PANI, POAP and poly(aniline-co-*o*-aminophenol) were synthesized electrochemically under potentiodynamic conditions at a scan rate of 50 mV/s. A three-electrode geometry was employed with gold sheets as working and counter electrodes and a saturated calomel reference electrode. The surface area of the working electrode was approximately 2.0 cm$^2$. All potentials quoted in this work are referred to the saturated calomel electrode. Electrochemical experiments were performed at room temperature with nitrogen-purged solutions. Cyclic voltammetry was performed with a custom built potentiostat connected to a computer with an AD/DA-converter interface.

For in situ conductivity measurements the polymer was deposited on a two-band gold electrode in a three-electrode cell with a specially designed electronic circuit supplying 10 mV DC voltage across the two gold strips as described elsewhere [33].

## Results and discussion

### Electrochemical homopolymerization of *o*-aminophenol and aniline

Figure 1 shows the electro-oxidation of OAP (1 mM) in 0.5 M $H_2SO_4$ solution when cycling the potential between −0.20 and 1.10 V at a scan rate of 50 mV/s. In the first positive sweep two peaks are well defined. The first peak observed at 0.67 V is caused by the oxidation of –OH of OAP and the other peak at 0.95 V is due to the oxidation of –NH$_2$ as has been reported earlier [31]. On the negative sweep none of these peaks show corresponding reduction peaks. On further potential cycling the oxidation current of these peaks decreased rapidly. However, no appreciable film growth was observed on the electrode surface but even after 100 cycles only brownish soluble products in the electrolytic cell. This might be due to the simultaneous degradation of polymeric materials at rather high anodic potentials. Similar cyclic voltammetric behavior was observed with higher concentrations of OAP in this potential range, except that the oxidation peak current on the first cycle was increased with increase in monomer concentration. Then a set of experiments was performed with gradually decreased upper potential limits and it was observed that reproducible POAP films could be deposited by cycling the potential between −0.20 and 0.84 V. Representative CVs (100 cycles) recorded during the homopolymerization of OAP (1 mM) by cycling the potential between −0.2 and 0.84 V at a scan rate of 50 mV/s are shown in Fig. 2a. As mentioned above there are two anodic peaks on the first cycle with no counterparts on the reverse scan which have been attributed to the oxidation of –OH and –NH$_2$ groups at the benzene ring. In the second cycle a redox pair was observed at 0.35/0.33 V. During continuous cycling it was observed that the system 0.35/0.33 V diminished slowly while anodic and cathodic currents increase in the potential region between −0.20 and 0.30 V. The redox system at 0.35/0.33 V has been attributed to the formation of a cyclic dimer of OAP, the 3-aminophenoxazone (3APZ), which is formed by a relatively slow cyclization reaction of the oxidized C–N dimer of the OAP cation radical [25]. The 3APZ thus formed plays the role of a monomer in the formation of POAP which results in the diminishing of the system at 0.35/0.33 V and corresponding growth of the polymer in the potential region between −0.2 and 0.30 V. These observations are in agreement with those reported on the growth of POAP on platinum electrodes [25]. The POAP modified electrode was then immersed into monomer free electrolyte solution and its CV (fifth cycle) was

**Fig. 1** Cyclic voltammograms for electrolysis of solution containing 1 mM OAP in 0.5 M H$_2$SO$_4$ by cycling the potential between −0.20 and 1.1 V at a scan rate of 50 mV/s
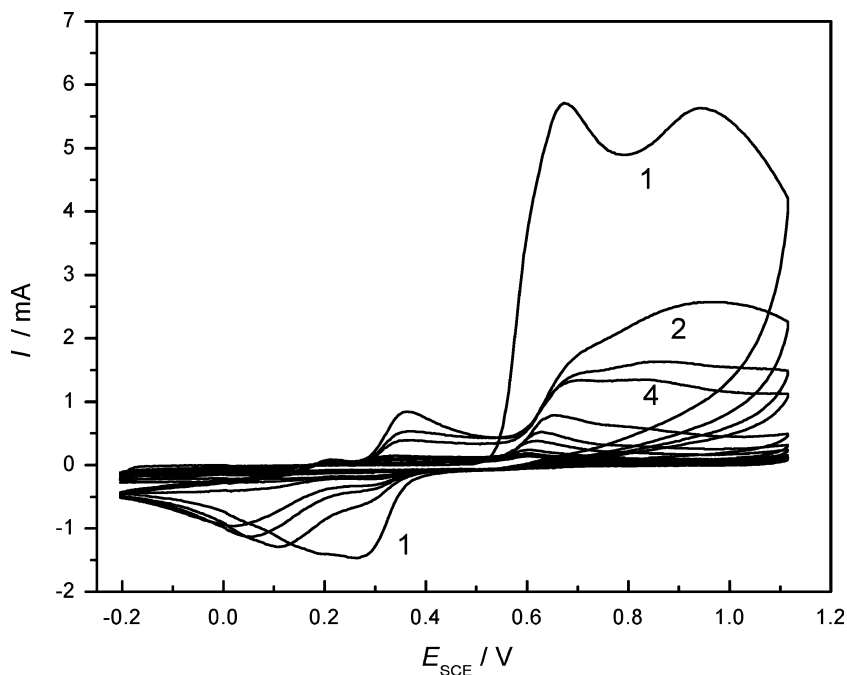


recorded in the potential range between −0.20 and 0.40 V as depicted in Fig. 2b. The film was brown in color and very stable; it did not lose its electrochemical activity after repetitive cycling both at very low and very high scan rates in this potential region.

Experiments were also carried out at higher concentrations of OAP ranging from 2 to 5 mM by cycling the potential between −0.20 and 0.84 V at a scan rate of 50 mV/s. The peak height of POAP in the monomer free electrolyte solution depends on the OAP concentration in the solution used in the electropolymerization, showing saturation at about 4 mM.

Aniline was also electrochemically polymerized by cycling the potential between −0.20 V and different upper potential limits. Figure 3a, b shows representative CVs (six cycles) recorded during the growth of a PANI film deposited from an aqueous solution of 20 mM ANI in 0.5 M H$_2$SO$_4$ by cycling the potential from −0.20 to 0.84 V and −0.2 to 1.1 V, respectively. On the first cycle there is only one anodic and one cathodic peak. On subsequent cycling three anodic and three cathodic peaks appeared. The peak currents of these peaks increase with the number of potential cycles. The peak at 0.15 V indicates the transformation of the reduced

**Fig. 2** The cyclic voltammograms for **a** electrolysis of the solution containing 1 mM OAP in 0.5 M H$_2$SO$_4$ by cycling the potential between −0.20 and 0.84 V and **b** POAP in monomer free electrolyte solution at a scan rate of 50 mV/s
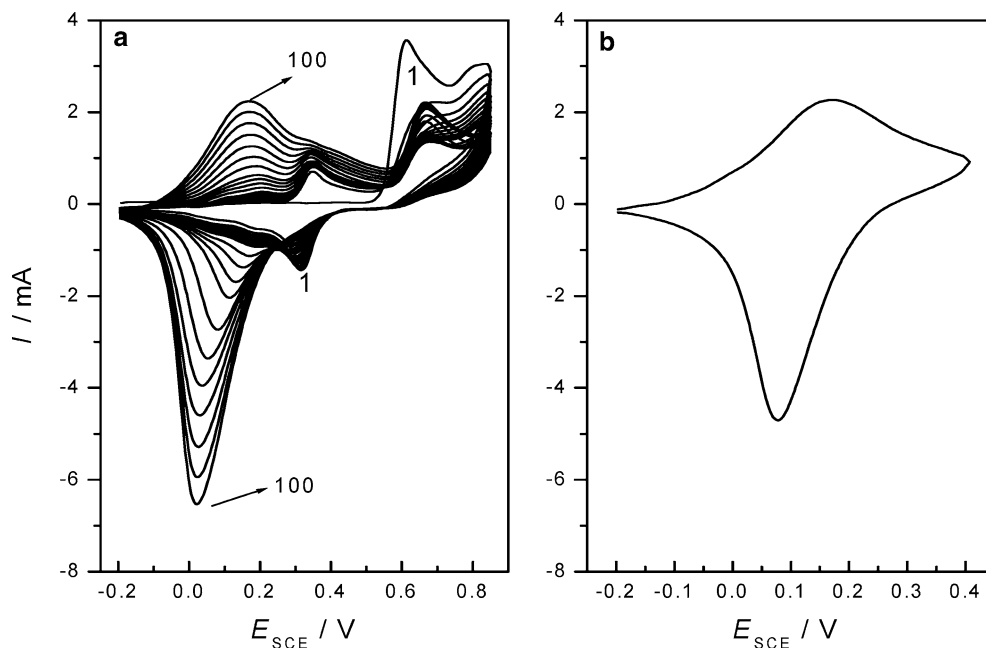
**Fig. 3** The cyclic voltammograms for electrolysis of solution containing 20 mM ANI in 0.5 M $H_2SO_4$ by cycling the potential between **a** −0.20 and 0.84 V and **b** −0.20 and 1.1 V at a scan rate of 50 mV/s
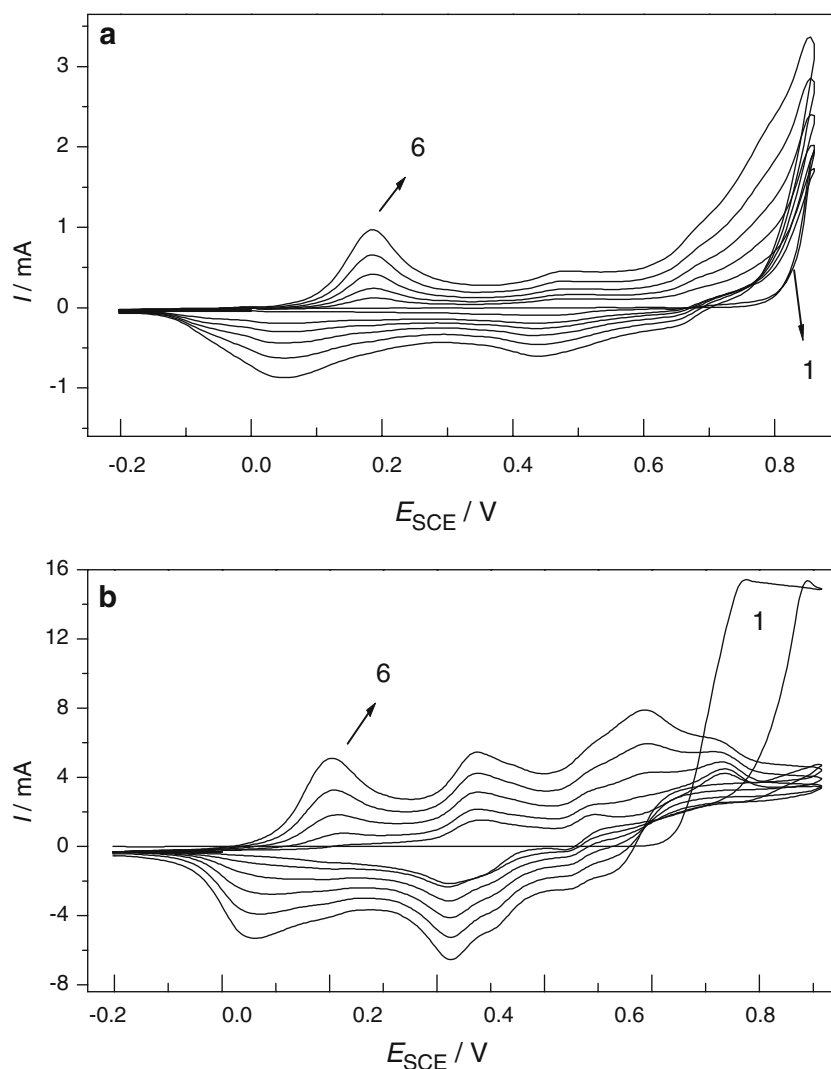


leucoemeraldine salt form into the emeraldine salt form; the peak at 0.80 V is assigned to further oxidation into the pernigraniline form. The middle peak is assigned to the presence of crosslinking of PANI caused by the reaction of nitrenium species being present as intermediates or to overoxidation products [34]. PANI film growth increases quickly with the increase of the upper potential limit but this also results in the increase of overoxidation products as evidenced by the middle peaks in Fig. 3b. After electrolysis a green colored film was observed on the working electrode.

Electrochemical copolymerization of aniline with *o*-aminophenol

Copolymerization was carried out with different feed concentrations of OAP and a constant concentration of ANI. The copolymers were labeled copolymer A (1 mM OAP + 20 mM ANI), copolymer B (2 mM OAP + 20 mM ANI), copolymer C (3 mM OAP + 20 mM ANI), copolymer D (4 mM OAP + 20 mM ANI) and

copolymer E (5 mM OAP + 20 mM ANI). Like the homopolymerization of OAP and ANI, electrolysis of mixed solutions containing both OAP and ANI was carried out by cycling the potential between −0.20 V and different upper potential limits. Unlike POAP deposition the polymer growth from mixed solutions was very slow when the potential was cycled between −0.20 and 0.84 V and increased with the increase of the upper potential limit from 0.84 to 1.1 V. However, polymer growth was not as rapid as that of the PANI deposition from the ANI solution alone.

Cyclic voltammograms recorded during the potentiodynamic copolymerization of ANI with OAP for system A are shown in Fig. 4a. There are two anodic and three cathodic peaks in the first cycle for copolymer A which is different from the first cycle of Figs. 1 and 3b. One anodic peak at 0.70 V can be assigned to the oxidation of the hydroxyl group of OAP. A further peak at about 1.0 V is caused by the oxidation of amino groups from both monomers. The three cathodic peaks on the reverse scan of the first cycle clearly indicate the deposition of the polymer with a behavior different from that
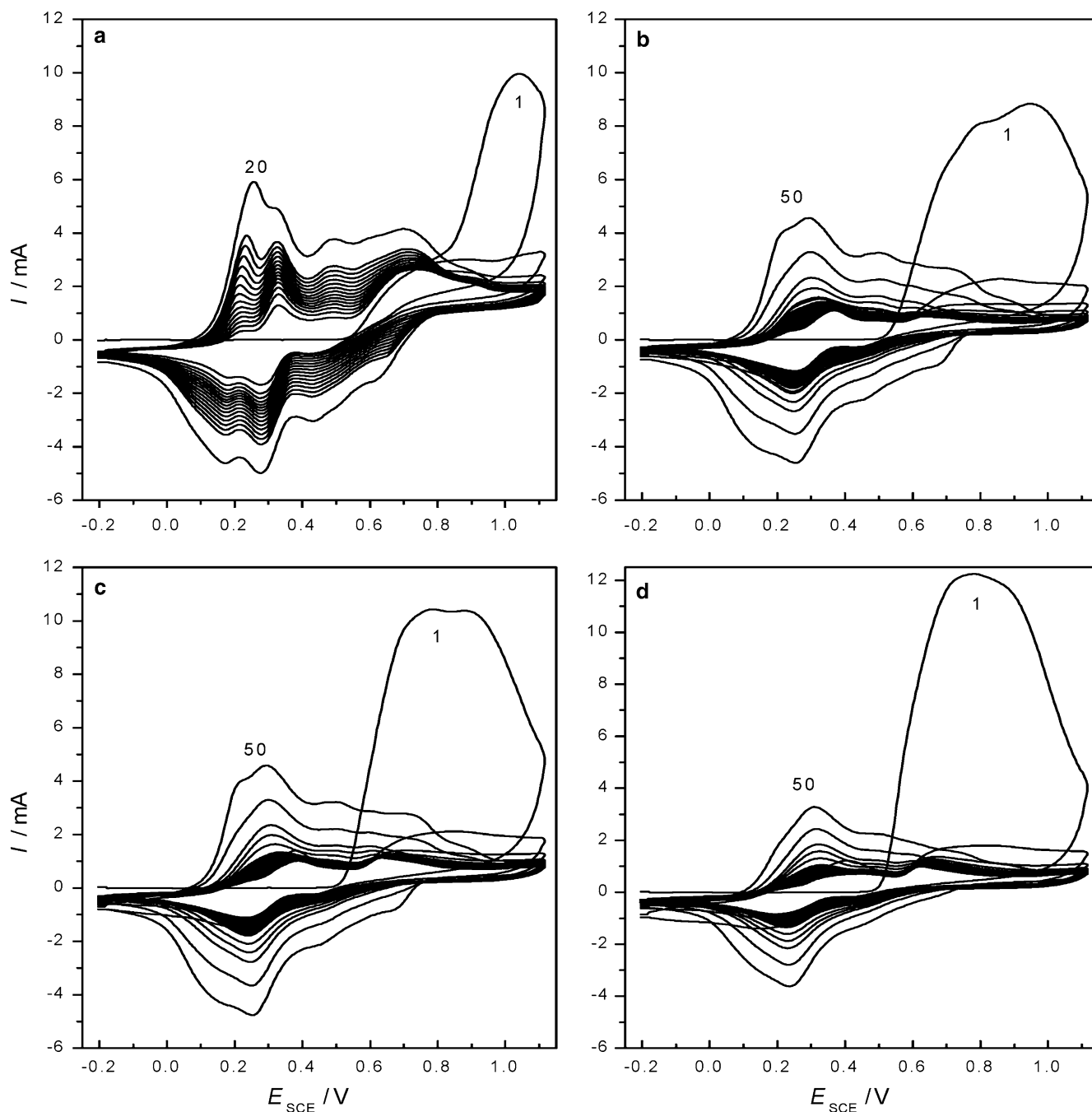
**Fig. 4** The cyclic voltammograms for the growth of **a** copolymer A (20 cycles), **b** copolymer B (50 cycles), **c** copolymer C (50 cycles) and **d** copolymer D (50 cycles) by cycling the potential between −0.20 and 1.10 V at 50 mV/s

of POAP and PANI. In the second cycle there are three anodic peaks, with a shoulder at 0.50 V, and four cathodic peaks. After the fifth cycle four redox pairs can be observed. Their peak currents increase with the number of potential cycles, at about one-third of the rate of increase of the peak currents observed during electrochemical polymerization of ANI (Fig. 3b). The overall electrochemical growth behavior of system A is different from the growth of PANI as an additional redox pair is present at 0.32/0.28 V in the CVs of the former

(Fig. 4a). This additional redox pair is caused by the copolymer itself and not by the oxidation and reduction of OAP on PANI films as no such peaks were observed when a PANI modified electrode was cycled in the solution for system A or OAP alone, between −0.20 and 0.45 or 0.50 V, respectively, at a scan rate of 50 mV/s. Moreover, a brownish-blue film was obtained on the working electrode, the color of which was different from the color of both homopolymers. These observations support the formation of the copolymer rather than the

formation of composite materials from both POAP and PANI.

Figure 4b shows the cyclic voltammetric behavior for the growth of the polymer from solution system B. There are two anodic and three cathodic peaks on curve 1 for the first cycle. One anodic peak at 0.77 V corresponds to the oxidation of the hydroxyl group of OAP, the second oxidation peak at 0.95 V is caused by the oxidation of amino groups from both monomers. The three cathodic peaks on the reverse scan indicate the deposition of a polymer. The first anodic peak is shifted towards the positive direction while the second one is shifted towards the negative direction as compared to the corresponding anodic peaks in the first cycle of co-polymer A. The main difference between curves 1 in Fig. 4a, b is the very quick decrease of the first oxidation peak in Fig. 4b in further potential cycling whereas in Fig. 4a it decreases only somewhat in the first two cycles and then increases on further potential cycling. In the second cycle there are four anodic peaks. The three anodic peaks at lower potentials correspond to cathodic peaks. In the following potential cycles both oxidation and reduction currents of these peaks (Fig. 4b) first decrease up to the fifth cycle and then increase slowly. Finally, a yellow colored film was observed on the working electrode.

Apparently the CVs recorded with the growth of copolymer C in Fig. 4c are almost the same as those recorded for copolymer B. The only difference can be observed in the first cycle. For copolymer B the anodic peak centered at 0.95 V is more prominent than the anodic peak at 0.77 V. In the case of copolymer C, both anodic peaks in the first cycle not only have the same current but also their peak currents are slightly higher than the corresponding peaks for copolymer B. Also the first oxidation peak of copolymer C is shifted towards the positive potential and is observed at 0.78 V while the second oxidation peak is shifted slightly more towards the negative potential and is observed at 0.90 V. However, the overall growth of copolymer C was slightly slower than that of copolymer B. These changes can be attributed to the influence of an increase in the OAP radical cation concentration. Figure 4d shows cyclic voltammograms for the electrolysis of solution system D. There are two anodic and three cathodic peaks on curve 1 for the first cycle. Further positive and negative potential shifts were observed for the first and second anodic peaks, respectively. In this case the first anodic peak appeared at 0.79 and the second anodic peak appeared at 0.88 V. Moreover, both of these peaks seem to merge into one. In the following potential cycles, both oxidation and reduction currents decrease very slowly up to seventh cycle, and then increase again. The overall growth of the copolymer was decreased further. The film color of copolymer D on the working electrode was deep yellow. In case of electrolysis of the solution system E (not shown), the voltammogram exhibits one sharp oxidation peak at 0.80 V in the first cycle. Copolymerization was strongly inhibited in this system. After pro-longed cycling a redox pair was observed in the potential region between 0.2 and 0.4 V, but the peak currents were considerably lower. Thus during polymerization, the influence of OAP radical cation concentration changed the potential, current and peak shape of the first cycle in particular and generally caused an inhibiting effect for copolymer growth. Based on the results presented, it can be concluded that the overall rate of electrochemical copolymerization decreases with increase in the molar fraction of OAP in combination with ANI.

Figure 5a shows the cyclic voltammogram of copolymer A along with the CV of PANI in 0.5 M $H_2SO_4$. The CVs were recorded after several potential cycles in the supporting electrolyte solution between −0.20 and 0.84 V until a stable CV was established. The cyclic voltammogram of PANI shows three redox couples as reported elsewhere [35]. The first redox couple at 0.17/0.03 V corresponds to the redox reaction between 'leucoemeraldine' and 'emeraldine', and the third redox couple at 0.70/0.67 V to the redox reaction between 'emeraldine' and 'pernigraniline'. The middle peaks of relatively low intensity observed at 0.46/0.42 V have been associated with degradation products present in the film. The CV pattern of the stabilized copolymer film is similar to the CV pattern obtained during copolymerization except the merging of the anodic peak at 0.33 V into the anodic peak at 0.26 V, to form a broad anodic peak at 0.24 V, along with the combination of the two corresponding cathodic peaks at 0.28 and 0.17 V into a current plateau which extends between 0.06 and 0.28 V. If the cathodic peak at 0.06 V in the plateau is assumed to belong to the PANI structure itself, then the other cathodic peak at 0.28 V (in the current plateau) can be attributed to the reduction of the quinoid structure in the copolymer film with the corresponding merged anodic peak in the broad anodic peak at 0.24 V. These observations were further supported by performing electrolysis of solution system A up to 30 consecutive cycles in the potential range of −0.20 to 1.1 V at scan rate of 50 mV/s, which resulted in the shifts of the anodic peak at 0.33 V towards the negative potential and finally merging into the anodic peak at 0.26 V to form a single anodic peak in the later stages of electropolymerization. However, the corresponding cathodic peaks at about 0.28 and 0.17 V were still observed in the later stages of copolymerization, which appeared in the form of a current plateau in the monomer free background electrolyte solution.

In comparison with PANI, CV of the copolymer reveals that the first redox couple is shifted by 0.10 V into the positive direction and the reduction peak of the first redox pair of PANI is also replaced by a current plateau between 0.06 and 0.28 V. Similarly the oxidation peak of the third redox couple of PANI at 0.70 V is replaced by a current plateau and the corresponding reduction peak is shifted towards lower potential. Figure 5b shows the stabilized CVs of all the copolymers in monomer free background electrolyte solution. The first oxidation peak in the copolymers B, C, and D appears in the form of a

**Fig. 5** The cyclic voltammograms of **a** PANI and copolymer A and **b** copolymers A–D in monomer free electrolyte solution between −0.20 and 0.84 V at 50 mV/s
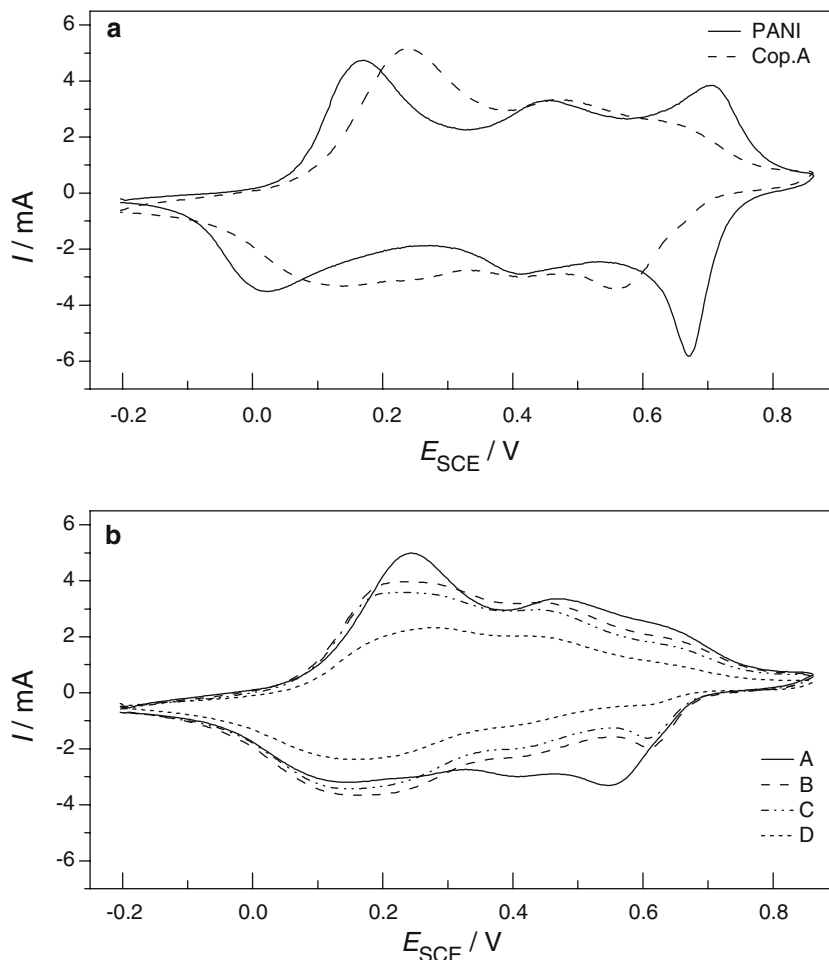


current plateau, between 0.19 and 0.28 V, rather than a broad anodic peak as with copolymer A. This observation clearly indicates the merging of two anodic peaks into one which appears as one broad anodic peak in the CV of copolymer A and in the form of a plateau in the CVs of copolymers B, C, and D in monomer free electrolyte solution. It is also noted that the current of the third redox couple diminished with the rise in the OAP content (copolymer D), as compared with that of the first redox couple. These observations suggest that the intermediate 'emeraldine' became unstable and most of the units in the copolymer were oxidized directly from 'leucoemeraldine' to 'pernigraniline' and reduced vice versa. Similar observations have been reported for copolymers of ANI with *o*-aminobenzonitrile [15].

Unlike POAP deposition, the rate of copolymerization greatly increases with the increase of the upper potential limit. Figure 6 shows the growth of the main anodic peak current on the potential cycling time, obtained at various upper potential limit values in solutions of different compositions. The greatest peak growth rate is attained at a low OAP to ANI ratio (copolymer A). On increasing the molar fraction of OAP in solution, a substantial decrease in the electropolymerization rate is observed.

### Effect of pH on the electrochemical activity of homopolymers and copolymers

Like PANI the copolymers show good electrochemical activity in acidic solution as displayed in Fig. 5. To study the role of the solution pH on the electrochemical activity, CVs of POAP, PANI and copolymers were recorded in 0.3 M $Na_2SO_4$ solution of different pH values ranging from 2.0 to 10.0. For this set of experiments homopolymers and copolymers were grown on the electrode surface to approximately the same thickness by adjusting predetermined experimental conditions. The electrochemical activity of the POAP film decreases very quickly as the pH of the $Na_2SO_4$ solution is increased from 2.0 to 4.0 as shown in Fig. 7a, which means that POAP is electrochemically active in acidic medium and retains its electrochemical activity only up to pH 4.0. With PANI and copolymers the electrochemical activity was also found to decrease with increasing pH from 2.0 to 4.0 (figure not shown), but the decrease was not as rapid as with POAP. However, changes were observed in the CVs of both PANI and copolymers while moving from pH 2.0 to pH 4.0, as there was only one anodic peak at about 0.15 V and one cathodic peak at 0.07 V in the CV of PANI at pH 4.0.

**Fig. 6** Dependence of the anodic peak current on potential cycling time, obtained in solutions of different compositions (**a–d**), as indicated in Fig. 4. Electrode potential has been cycled within the limits of −0.2 to 0.84 V (*filled circle*), −0.2 to 0.9 V (*filled diamond*) and −0.2 to 1.1 V (*filled triangle*)
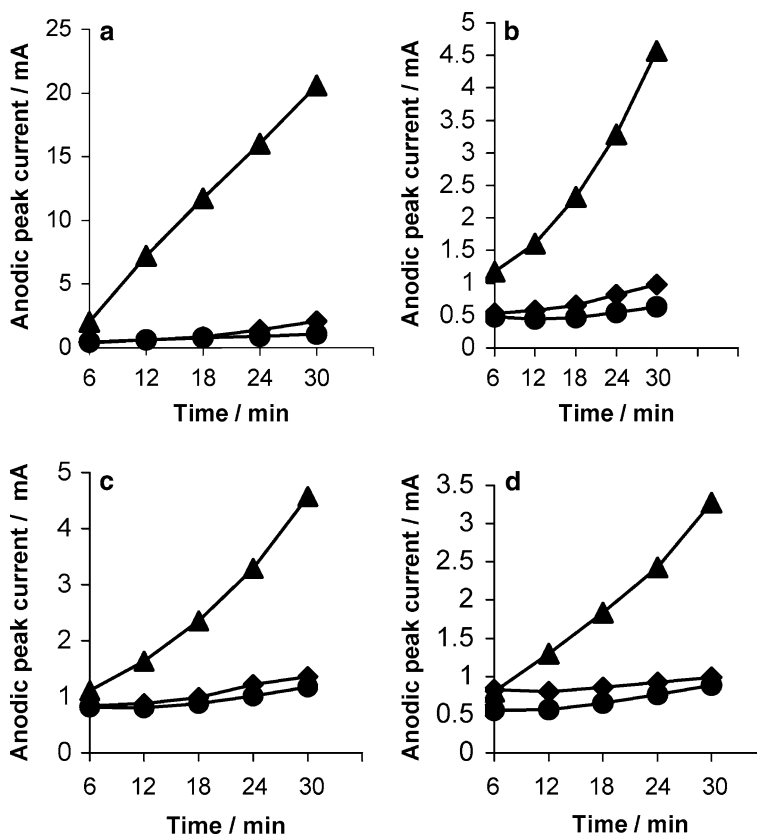


On the other hand the CVs of copolymers A and B showed a broad anodic peak at about 0.06 V and a broad cathodic peak at about 0.00 V at pH 4.0. However, the anodic and cathodic peak currents were higher in copolymers A and B than the peak currents of PANI at pH 4.0. Quick changes in the electrochemical activity were observed while changing the solution pH from 4.0 to 10.0. Figure 7b–f shows the CVs of PANI and copolymers A–D in an aqueous solution of 0.3 M $Na_2SO_4$ adjusted to different pH values ranging from 5.0 to 10.0 There is still one anodic peak at 0.15 V and one cathodic peak at 0.07 V in the CV of PANI at pH 5.0. However, the oxidation peak vanishes at pH 7.0. Based on the changes in oxidation and reduction currents with pH values, it is observed that the electrochemical activity of PANI decreases quickly as the pH value increases from 5.0 to 7.0. This result, shown in Fig. 7b, indicates that PANI has little electrochemical activity at pH > 4.0 and its useful potential range decreases with increasing pH value. The CVs of copolymers A–D (Fig. 7c, d) are different in shape from that of PANI at the same pH values. Although no sharp peaks occur, a broad anodic peak at about 0.60 V and a broad cathodic peak at about 0.00 V appear for both copolymers A and B. The anodic peak currents decrease slowly with increase in pH values from 5.0 to 10.0. This indicates the slow decrease in the electrochemical activity of these copolymers with increasing pH. Broad anodic and cathodic peaks were observed at 0.40 V, −0.05 V and 0.30 V, −0.10 V for copolymers C and D, respectively (Fig. 7e, f). The peak

currents of copolymer C decrease quickly as compared to copolymers A and B but not as rapidly as with PANI in the pH range 5.0–10.0. However, the electrochemical activity of copolymer D vanishes very quickly with increase in pH. The results from CVs of the copolymers (at least in the case of copolymers A and B), from pH 5.0 to 10.0, indicate that the films are still electroactive at pH values higher than 5.0 as compared to the respective homopolymers. This has been interpreted in terms of the presence of –OH groups in the copolymer chain [31]. Phenol can be oxidized to quinone and quinone can be reduced to phenol. This reversible redox process must be accompanied by a proton exchange between the copolymer and the solution, which plays an important role in adjusting the pH value in the vicinity of the copolymer-coated electrode. Therefore, the electrochemical activity of the copolymers at pH > 4.0 is mostly attributed to the substituent –OH groups in the copolymer chain. However, this explanation also creates a question about the proposed structure of the polymer and the incorporation of OAP units into the polymer chain. If the copolymer contains –OH group-substituted phenyl rings in the PANI backbone and the proportion of the OAP unit increases in the copolymer with increase of OAP concentration in the monomer feed during electrolysis, then the electrochemical activity of copolymer D should be better than copolymer C which in turn should be better than copolymers B and A, respectively, in the pH range studied. However, this is not the case in our study. So the structure of poly(aniline-co-*o*-amino-

**Fig. 7** CVs recorded in 0.3 M sodium sulfate solution with various pH values (as indicated) for POAP (**a**), PANI (**b**), copolymer A (**c**), copolymer B (**d**), copolymer C (**e**) and copolymer D (**f**)
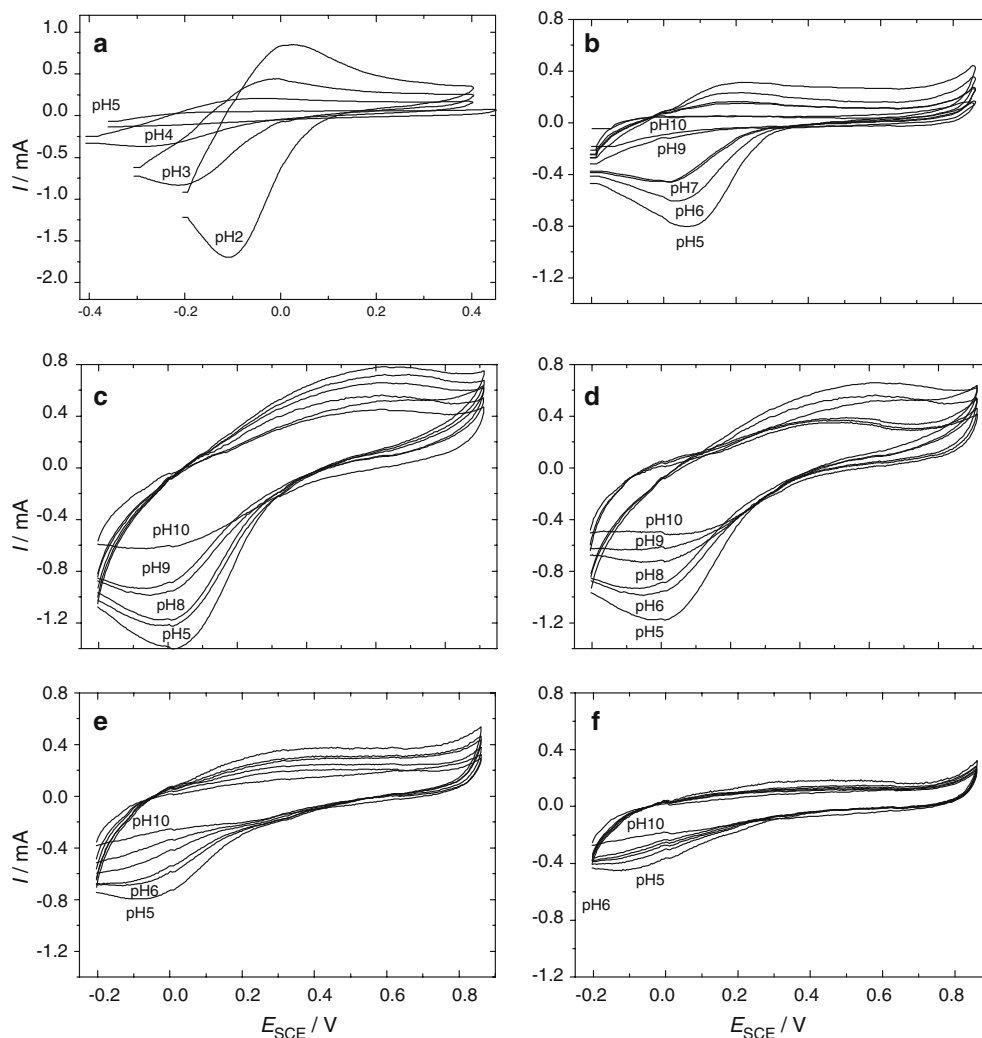
phenol) is not as simple as had been assumed and a more complex situation must be considered. Therefore, further investigation is in progress in our laboratory in an effort to determine the role of OAP in the polymerization process by using in situ spectroelectrochemical techniques.

Electrochemical synthesis of polyaniline over poly(o-aminophenol) modified electrode

Figure 8 shows CVs recorded during the first and subsequent potential sweeps of a POAP-coated electrode in an ANI solution. Previously the POAP modified electrode was prepared by cycling the potential between −0.20 and 0.84 V in a solution of 2 mM OAP at a scan rate of 50 mV/s (100 cycles). In the first sweep there are anodic and corresponding cathodic peaks at 0.10 and 0.05 V, respectively, which are similar to those obtained with POAP in 0.5 M $H_2SO_4$ solution. An additional anodic peak can be observed at about 0.84 V, which obviously corresponds to ANI electro-oxidation. The latter peak is markedly lower than the one observed with

a bare gold electrode, indicating a lower rate of ANI radical cation formation at anodic potentials on an electrode already covered with a POAP layer. This might be in part caused by the slightly poorer conductivity of POAP at this electrode potential. Alternatively this might indicate partial blocking of the electrode surface by POAP, thus only a fraction of the gold surface (not covered by POAP) might be available for ANI oxidation. In the subsequent five sweeps the anodic peak at 0.10 V expands into a plateau between 0.10 and 0.18 V with no appreciable change in the peak current. On the other hand the corresponding cathodic peak current not only decreases but is also shifted slightly towards higher potentials. An additional peak starts to develop at 0.50 V in the fifth sweep. In the subsequent sweeps the end of the plateau at 0.10 V diminishes slowly, while the end at 0.18 V grows with potential cycling and appears as an anodic peak as evident in the tenth sweep. However, the current of the corresponding cathodic peak decreases and the peak is further shifted towards higher potential. Meanwhile, another cathodic peak, corresponding to the anodic peak at 0.05 V, can be observed in the tenth sweep. In the following sweeps, i.e. from the
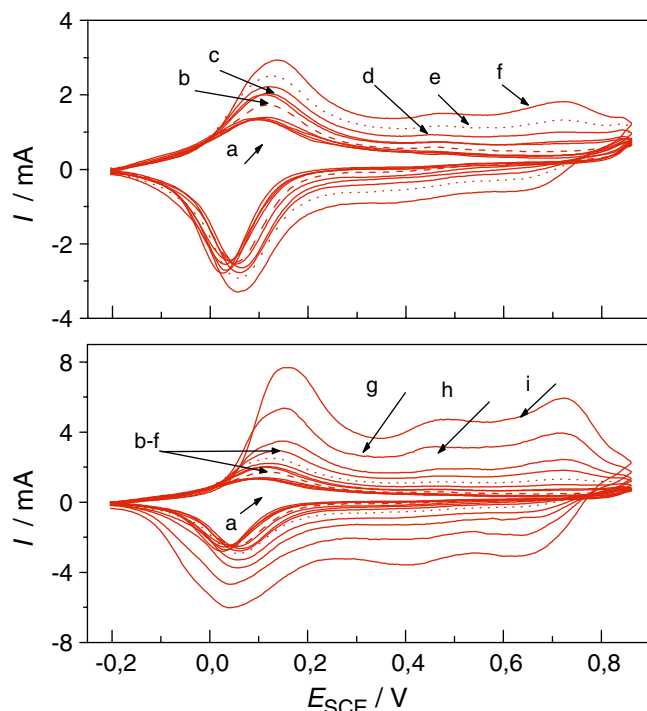
**Fig. 8** CVs of a POAP-coated electrode in 20 mM ANI solution in 0.5 M sulfuric acid within potential sweep limits of −0.20 and 0.84 V: number of cycles is: *top* **a** 1–5, **b** 10, **c** 15, **d** 20, **e** 25, **f** 30; *bottom* **a**–**g** 35, **h** 45 and **i** 55. Previously the POAP modified electrode was prepared by cycling the potential between −0.20 and 0.84 V in 2 mM OAP at a scan rate of 50 mV/s (100 cycles)

tenth onwards, the anodic peak current at 0.18 V increases linearly, but the corresponding cathodic peak current increases instead of decreasing and the peak is also shifted towards lower potentials as seen in the 15th sweep. An additional anodic peak at 0.80 V with a corresponding cathodic peak at 0.74 V is also observed in the 15th sweep. In subsequent potential scans the voltammograms gradually assume the form typical for PANI on a metallic support. The whole process of PANI deposition over POAP seems to consist of three stages:

1. ANI electro-oxidation,
2. Formation of PANI/POAP composite or copolymer formation, and
3. PANI growth at the copolymer/solution interface.

The suppression of peaks of the POAP and PANI/POAP redox activity in stages 2 and 3 is probably due to redistribution of potential in the polymer coating with the increasing thickness of PANI caused by different mechanisms and rates of charge transfer in PANI and POAP. From a kinetic point of view, redox processes on POAP, PANI/POAP and PANI are different. At potentials of anodic synthesis of PANI over POAP, the latter is undoped and the potential drop occurs predominantly at the metal/polymer interface and in the polymer bulk [36], suggesting that PANI in stage 2 is deposited into the POAP bulk. Once some

PANI is deposited, the PANI/POAP layer acquires electron-conducting properties, the potential alters at the polymer/solution interface and ANI polymerization takes place at the interface.

### First cycle effect in PANI-coated and POAP-PANI-coated electrodes

One of the interesting features of the voltammetric response of most conducting and some electroactive polymers is the occurrence of the so-called 'first cycle effect', 'memory effect' or 'slow relaxation' [34, 37, 38]. This refers to the fact that a polymer kept at an electrode potential in its reduced state for some time shows a voltammetric profile during the first positive going half cycle different from the steady-state profile. The first wave of a CV always differs in shape and peak position from the following ones [39], and oxidation charge passed in the first cycle is larger than in the subsequent cycles [40].

Figure 9a shows CVs of a PANI-coated electrode, recorded after holding the electrode at $E = 0.05$ V, for 0 and 60 s, respectively. The PANI-coated electrode was prepared by 25-fold potential cycling between −0.20 and 0.84 V in 0.5 M sulfuric acid containing 20 mM ANI. It is obvious that the anodic peak obtained after holding the electrode at a potential corresponding to a fully reduced PANI form (leucoemeraldine) is about 1.5-fold higher and shifted by 0.025 V towards the higher potential, as compared to that recorded without the waiting period (0 waiting time). Figure 9b shows CVs of a POAP-PANI-coated electrode, which contains an electropolymerized POAP layer under a PANI film, obtained after holding the electrode at 0.05 V after waiting times of 0 and 60 s. The electrode was prepared by 15 potential cycles between −0.20 and 0.84 V in 0.5 M sulfuric acid containing 2 mM OAP, and subsequent 30-fold potential cycling within the same potential limits in 0.5 M sulfuric acid containing 20 mM ANI at a scan rate of 50 mV/s. It presents an almost similar picture as that obtained with the PANI-coated electrode. However, in this case the first cycle effect is less pronounced than in the former case, i.e. the anodic peak is about 1.35-fold higher as compared to that obtained without the waiting period. Also, with thicker underlying POAP layers, this effect is further decreased as depicted in Fig. 9c, d, where the POAP-PANI modified electrodes were prepared by 30- and 50-fold potential cycling between −0.20 and 0.84 V in 0.5 M sulfuric acid containing 2 mM OAP, and subsequent 30-fold potential cycling within the same potential limits in 0.5 M sulfuric acid containing 20 mM ANI, respectively.

The memory effect manifests itself only after holding the electrode for some time at a potential less positive than that of the leucoemeraldine–emeraldine transition. No effect is observed with the electrode kept at an open circuit potential. Figure 10a shows the dependence of the anodic peak current on the waiting time after hold-

**Fig. 9 a** CVs of a PANI-coated electrode in 0.5 M sulfuric acid after holding the electrode at $E = 0.05$ V for waiting times of 0 and 60 s. The PANI-coated electrode was prepared by 25-fold potential cycling between $-0.20$ and 0.84 V in 0.5 M sulfuric acid containing 20 mM ANI. **b** CVs of the POAP-PANI-coated electrode after waiting times of 0 and 60 s. The electrode was prepared by 15-fold potential cycling between $-0.20$ and 0.84 V in 0.5 M sulfuric acid containing 2 mM OAP, and subsequent 30-fold potential cycling within the same potential limits in 0.5 M sulfuric acid containing 20 mM ANI. Other conditions as above. **c** and **d** same as in (**b**), except that the POAP-PANI-coated electrodes were prepared by 30- and 50-fold potential cycling in OAP solution and subsequent 30-fold cycling in ANI solution, respectively
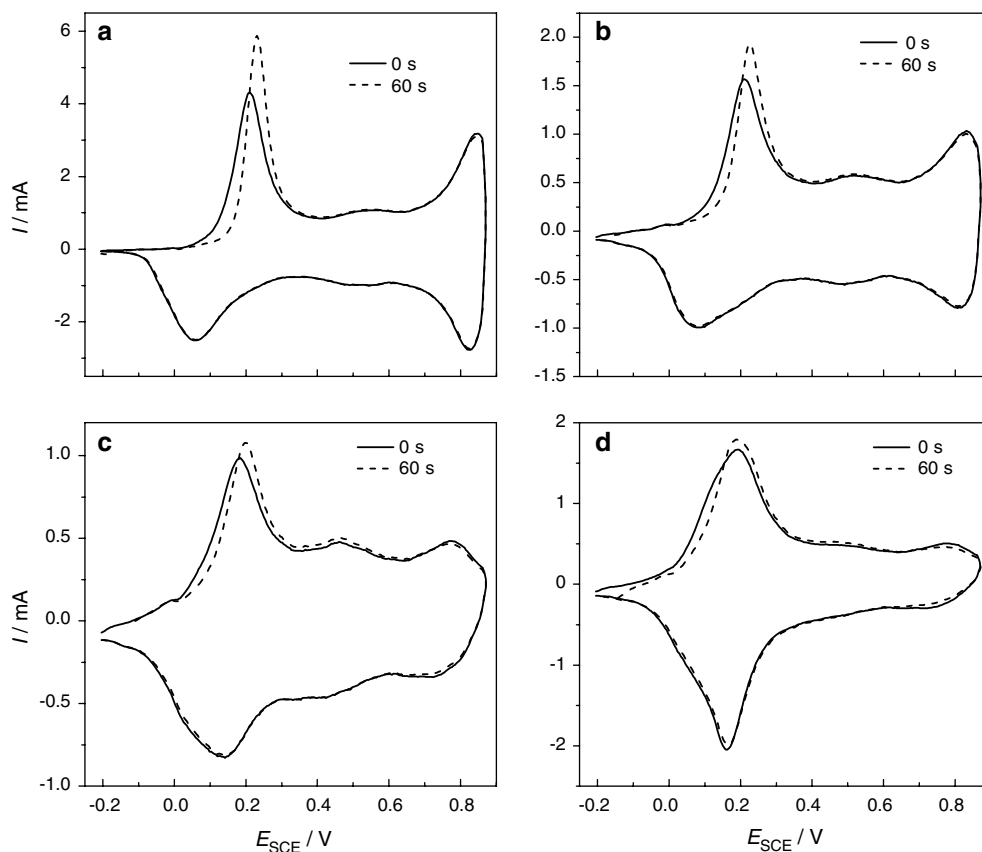
ing a PANI-coated electrode at various potentials. It can be seen that the anodic peak current increases with the waiting time and reaches a maximum value when the electrode is kept at 0.05 and 0.10 V, respectively. However, for higher potentials, i.e. 0.20 and 0.25 V, neither an increase in the peak current nor a shift of the peak were observed. The dependence of the anodic peak currents on the waiting time after holding POAP-PANI-coated electrodes, which differ in the thickness of the underlying POAP layer, at various potentials is shown in Fig. 10b–d. With a thin underlying POAP layer (cf. Fig. 10b), the behavior is similar to that of a PANI-coated electrode. However, for thick underlying POAP layers very little effect can be seen only at 0.05 V (Fig. 10c, d). These results are different from those obtained with poly(o-phenylenediamine) (POPD) underlying layers where an enhanced 'first cycle effect' has been reported [21].

Inzelt [41] and Pruneanu et al. [42] reported that in acidic solutions in the first stage of PANI oxidation a deprotonation occurs and the proton leaves the film. At the later stage of oxidation anions go into the PANI film. However, during POAP oxidation, the incorporation of anions at less positive potentials and the expulsion of protons from the polymer at more positive potentials are produced simultaneously [29].

It is interesting that during POAP oxidation anions are incorporated into the polymer film whereas during PANI oxidation deprotonation of the film takes place at less positive potentials. This phenomenon is expected to help in understanding the decrease of the 'first cycle effect' in polymers containing both POAP and PANI. During anodic potential sweeps with a POAP-PANI-coated electrode, oxidation of the POAP layer proceeds first and reaches a maximum rate at $E = 0.0$–$0.20$ V. Simultaneously, anions are incorporated into the polymer from the acidic electrolyte solution. In further potential sweep oxidation of the PANI layer begins with a current peak at $E = 0.10$–$0.30$ V. Since both oxidation processes occur at almost the same potential, it takes only about a second to sweep the electrode potential from the POAP to the PANI oxidation process. Thus the decrease in the concentration of anions, which is caused by POAP oxidation, will result in the corresponding increase of proton concentration in the electrolyte solution. As POAP and PANI layers are located in very close proximity on a POAP-PANI-coated electrode, a low local anion concentration formed during POAP electro-oxidation should increase the proton concentration which should in turn slow down the anodic oxidation of PANI. Thus if deprotonation of a PANI film is assumed to be the rate-determining step in the course of anodic oxidation of leucoemeraldine to emeraldine, a decreased local anion concentration formed during a preceding POAP electro-oxidation can decrease the rate of deprotonation of the PANI film which can cause the decrease in the peak current of the first PANI electro-oxidation process, i.e. the decrease of the 'first cycle

**Fig. 10** Dependence of the anodic peak current on the waiting time after holding the electrode at different potentials (as indicated) in 0.5 M sulfuric acid for electrodes as described in Fig. 9
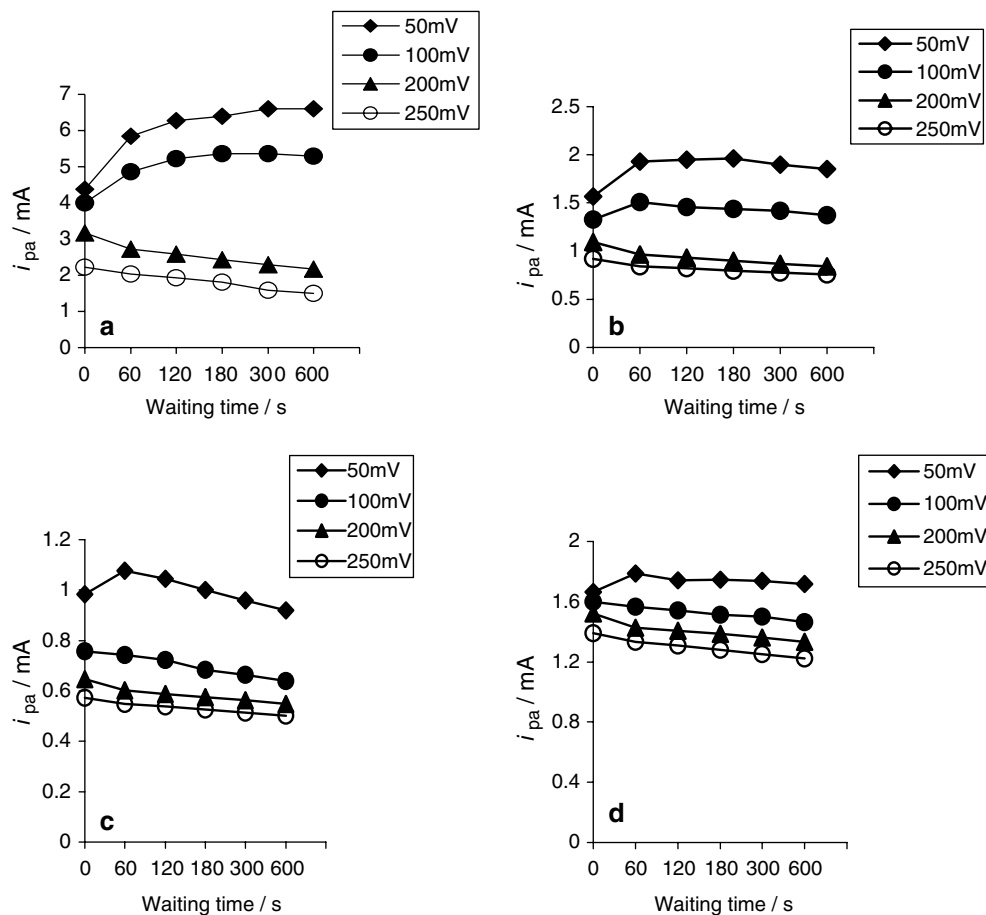


effect' in a POAP-PANI bilayer structure, which contains an additional POAP layer between the electrode and PANI film. A thicker underlying POAP layer leads to further decrease of the PANI peak current since a further decrease in the anion concentration should be created during electro-oxidation of a thicker POAP layer.

In situ conductivity

For in situ conductivity measurements PANI, POAP and copolymers were deposited potentiodynamically on an Au bandgap electrode. In this electrode the two gold strips are separated by a gap of a few micrometers that is easily bridged through deposition of conducting polymers, when both electrodes are connected electrically together and used as the working electrode. Although this set-up is associated with the problem of ensuring the identical thicknesses of films across the insulating gap, nevertheless, approximately reproducible results can be obtained by adjusting the experimental conditions as very thin films can usually form good bridges over the gap between the electrodes. During in situ conductivity measurements the electrodes are connected to the measurement circuit. Electrochemically induced changes in the polymer can be obtained by applying appropriate

electrode potentials to both electrodes which are then connected together as the working electrode. Alternate potential changes and conductivity measurements are facilitated as soon as the electrode set-up is connected to the electrochemical potentiostat and the measurement circuit via a double pole switch. To ensure good bridges over the gap cyclic voltammograms of the deposited polymer films on the bandgap electrode were recorded before each series of conductivity measurements in the electrolyte solution.

The resistivity versus the applied electrode potential plot of PANI in 0.5 M $H_2SO_4$ is displayed in Fig. 11a. PANI shows two changes in resistivity. When the applied potential is increased, the resistivity of PANI decreases sharply by 2.5 orders of magnitude at 0.10 V and then increases again at 0.65 V. When the potential shift direction is reversed from 0.80 to −0.20 V, the resistivity of PANI is almost restored. In the case of POAP in situ conductivity was only observed in the potential region between −0.10 and 0.10 V (Fig. 11b), but lower by 4.2 orders of magnitude than with PANI. At a more positive electrode potential the resistivity increased beyond the initial value; during the negative going potential scan it returned to the initial value.

Low in situ DC conductivity has been reported for POAP elsewhere [32, 43]. Results obtained with copolymers A, B and D are shown in Fig. 11c–e. When
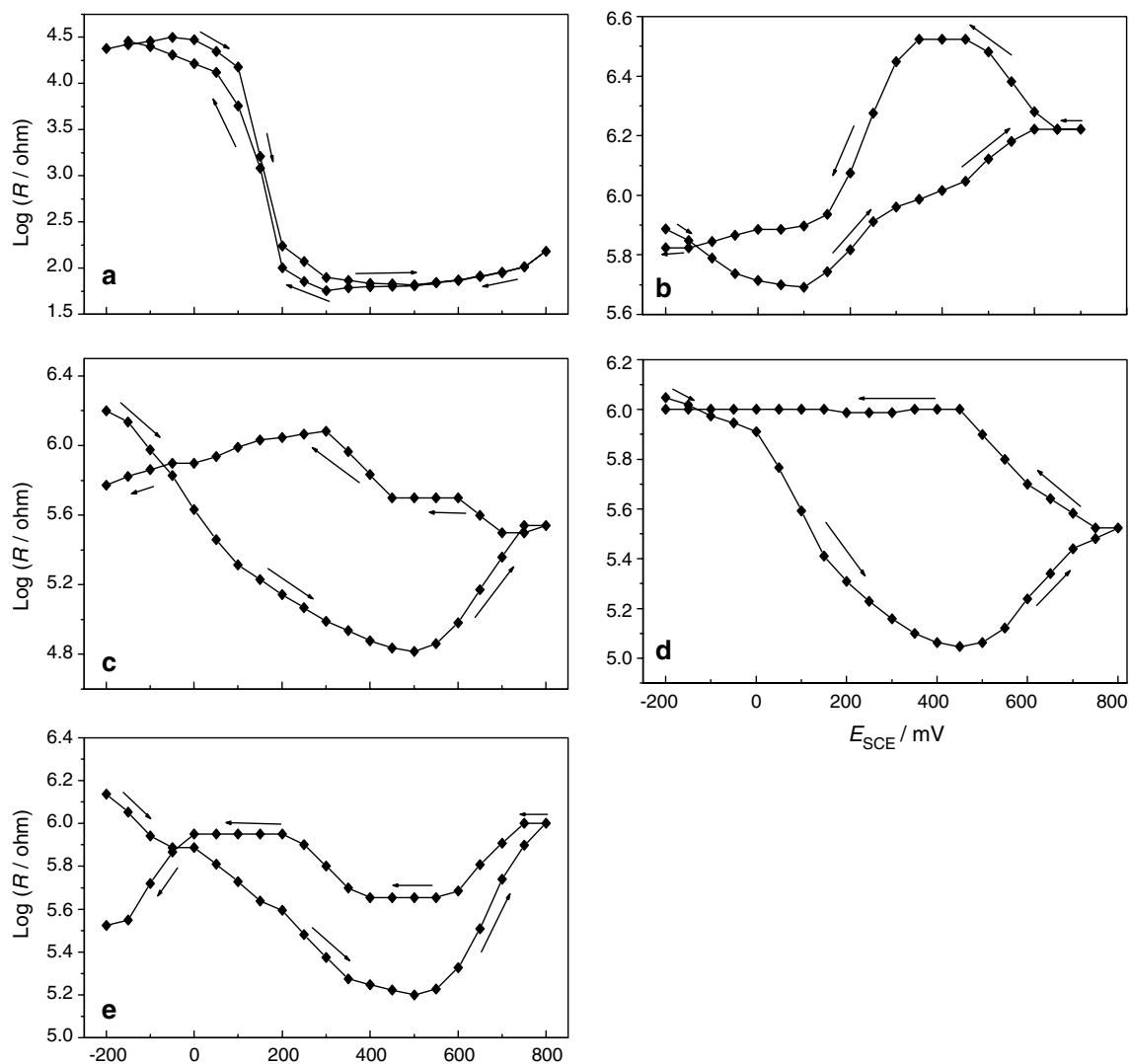
**Fig. 11** Resistivity versus electrode potential data for PANI (**a**), POAP (**b**), copolymer A (**c**), copolymer B (**d**) and copolymer D (**e**)

the applied potential is increased, the resistivity of copolymer A decreases at −0.10 V slowly and then increases at 0.55 V. Minimum resistivity can be observed in the range between 0.40 and 0.55 V. Its conductivity is lower than that of PANI by 2.8 orders of magnitude. Like copolymer A, two changes can be observed with copolymers B and D. However, their resistivities are further lowered by 3.1 and 3.2 orders of magnitude, respectively, as compared to PANI.

As with PANI, two transitions were observed in the conductivity behavior of all the copolymers studied. However, the resistivities of the copolymers were not restored when the potential shift direction was reversed from 0.80 to −0.20 V. This might be due to degradation of the copolymer at high potentials. Based on these observations the in situ conductivity behaviors are not the sum of those of the two individual homopolymers, but seem to be determined by the ANI fraction in the copolymer. The considerable drop in overall conductivity even at the smallest POA-content indicates that

POA-units interrupting undisturbed PANI-chains may be present rather frequently on the molecular chains; this suggests a statistical copolymer which of course contains extended blocks of PANI because of the high ANI fraction.

## Conclusions

Copolymers of ANI and OAP have been prepared potentiodynamically in a solution containing 0.5 M $H_2SO_4$, 20 mM ANI and different concentrations of OAP. The copolymers formed with different feed concentrations of o-aminophenol exhibited different cyclic voltammetric behaviors and various color changes were observed during the copolymerization. The synthesized poly(aniline-co-o-aminophenol) films showed good adherence and were found to be electrochemically active even at a pH = 10.0. The first redox couple of the leucoemeraldine–emeraldine transition for the copolymer

has a midpoint potential of 0.25 V and is shifted by about 0.10 V to the positive direction, as compared to PANI. In situ resistivities of the copolymers were higher by 2.8–3.2 orders of magnitude as compared to PANI.

Electrochemical studies of PANI electrosynthesis on the POAP-coated electrode showed the passing of three stages: reaction initiation, copolymer formation and formation of a PANI layer at the copolymer/solution interface. A decrease in the 'first cycle effect' was observed on PANI-coated electrodes, when an additional POAP layer was placed between the electrode and the PANI layer.

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