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The Effect of Anodic Surface Treatment on the Oxidation of Catechols at Ultrasmall Carbon Ring Electrodes

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A-1

THE EFFECT OF ANODIC SURFACE TREATMENT ON THE OXIDATION OF CATECHOLS AT ULTRASMALL CARBON RING ELECTRODES

ABSTRACT

Electrochemical anodic treatment at ultrasmall carbon ring electrodes appears to result in the formation of an oxide film which displays charge-selective and pH dependent enhancements following treatment. Voltammetry after treatment in pH 7.4 citrate-phosphate buffer is more Nernstian for dopamine (DA) and less Nernstian for 3,4-dihydroxyphenylacetic acid (DOPAC). However, oxidation in pH 2.8 buffer gives rise to voltammetry which is less Nernstian for both DA and DOPAC. Extensive surface oxidation in potassium hydroxide apparently forms a thick layer which acts like a thin layer reservoir for adsorbed analyte. Voltammetry following extensive treatment is attenuated and peak shaped. Minimal surface oxidation in KOH results in more Nernstian sigmoidal voltammetry with only slight current attenuation. The data suggest that an oxide layer formed following anodic treatment is non-uniform and leaves sites of activated carbon exposed on the surface. Furthermore, it appears that this layer has cation-exchange properties giving rise to charge transfer selectivity. A model of the surface formed following anodic oxidation is consistent with previous models involving both surface cleanliness and carbon structure orientation.

INTRODUCTION

Because of the vast electroanalytical utility of carbon electrodes, the mechanism of electron transfer at carbon surfaces has been widely studied (1). Of particular interest to investigators is the mechanism responsible for activation of carbon electrodes. Electrode activation has been employed to improve the response of electrodes used for detection in liquid chromatography (LCEC) (2), microelectrodes used for <u>in vivo</u> voltammetry (3,4), and is necessary for sensitive analysis. Various treatments, devised in order to improve the electrochemical response, have included exposure to radio-frequency plasma in an oxygen atmosphere (5,6), laser irradiation (7-9), heat treatment (10-12), and electrochemical treatment (2-4,13-22). Several theories have emerged in the literature which attempt to explain the activation mechanism. Among the activation theories, three which have gained considerable attention are activation resulting from surface cleaning, from mediation by surface functional groups, or from enhanced charge transfer rate due to modification of the carbon structure.

Electron transfer enhancements following heat activation have been explained by an increase in the density of active sites by removal of surface impediments and the exposure of fresh carbon (12). Other investigators have speculated that electrochemical treatment also results in removal of surface impurities (10,13,14,18,21,22). In addition to simply removing contaminants from the surface, the production of surface functionalities during electrochemical treatment has been associated with enhanced electron transfer (10,13-15,23). McCreery and co-workers have proposed that electron transfer enhancements following either laser irradiation or electrochemical anodic treatment result primarily from desorption of impurities and formation of graphitic carbon edge planes (25-27). Using micro Raman techniques on highly ordered pyrolytic graphite, they have shown that the absorbance at 1360 cm^{-1}, indicative of a carbon edge plane surface, dramatically intensifies after laser irradiation and anodic treatment. More recently, Bard and co-workers have reported the formation of a graphitic oxide film following electrochemical treatment and have associated it with activation of the electrode (28,29). Beilby and Carlsson have also classified the film formed following anodic treatment as graphite oxide (30). Others have considered the effect of surface coverage on the electrochemical response. Wightman and co-workers showed that electrochemical treatment results in a partially blocked electrode surface with coverage resulting from formation of an insulating oxide layer (31). Theoretical treatments of partially blocked electrode surfaces before and after electrochemical treatment have been explored by several investigators (32-36). It was found that partial coverage of the electrode by adsorbed substances blocking the transfer of electrons may result in a decreased apparent rate of electron transfer (33).

Our group has reported the effect of electrochemical treatment of carbon ring electrodes and demonstrated a unique charge selective activation (37). Following anodic treatment, voltammetry of catechols with positive side chains becomes more reversible, voltammetry of neutrals shows little change, and voltammetry of negatively charged catechols becomes less reversible at carbon ring electrodes. This behavior has been attributed to a specific electrostatic interaction at the molecular level between the carbon surface and the molecule side chain. In this paper, the effects of electrochemical treatment on carbon ring electrodes in basic, neutral and acidic solutions are discussed. The data have been used to develop a model for the electrode surface which might explain the unique behavior of carbon ring electrodes following electrochemical treatment.

EXPERIMENTAL

Chemicals and solutions. Citrate-phosphate McIlvaine buffers (pH 7.4 and 2.8, 0.5 M ionic strength), made with distilled water and adjusted with HCl, were used to prepare solutions daily. Dopamine hydrochloride (DA), 4-methylcatechol (4-MC), and 3,4-dihydroxyphenylacetic acid (DOPAC) (Sigma Chemical Co.) were used as received. Solutions were thoroughly deaerated with nitrogen and kept under nitrogen between voltammetric scans.

Electrodes and apparatus. Carbon ring electrodes were constructed as described previously (38) with one adjustment. The upper portion of the quartz barrel was filled with colloidal graphite to provide electrical contact with the carbon film. A piece of 30-gauge nichrome wire was then placed into the colloidal-graphite-filled barrel.

Cyclic voltammetry was carried out with a locally constructed low-current three electrode potentiostat and waveform generator. The electrochemical cell consisted of a 30-mL glass vial with three holes drilled in the lid to accommodate the three electrode system. A sodium saturated calomel electrode (SSCE) served as the reference electrode, and a nichrome wire served as the auxiliary electrode.

Wave slopes were determined by plotting E vs log $(i_l-i)/i$. Because voltammograms at carbon ring microelectrodes frequently do not give perfectly horizontal limiting currents, the following procedure was used for finding the limiting current. A tangent was drawn along the most linear section of the upward rising portion of the voltammogram. Another tangent was drawn along the 'steady state' portion of the curve. A third line which bisects the angle formed by these two lines was drawn. The point of intersection of the bisecting line on the voltammogram was then used as the normalized limiting current.

Electrochemical treatment. Where indicated, carbon electrodes were treated by cycling the potential between -0.2 V and 1.8 V at 200 or 400 mV/s in the following solutions as indicated: deoxygenated solution containing only pH 7.4 or 2.8 citrate-phosphate buffer (0.5 M ionic strength) or a solution of potassium hydroxide (KOH) at 0.003, 0.03, 0.3, or 3 M. One reference electrode was specifically dedicated for treatment in KOH.

RESULTS AND DISCUSSION

Effect of pH on voltammetry following electrochemical treatment. Saraceno and Ewing have demonstrated that electrochemical treatment of carbon ring electrodes in pH 7.4 citrate-phosphate buffer results in an activated surface for voltammetry of cationic catechols and a deactivated surface for anionic catechols (37). A charge selective adsorption prior to electron transfer was suggested as the mechanism. In order to test this hypothesis, the voltammetry of DA and DOPAC have been compared after anodically treating the electrode in both neutral (pH 7.4) and acidic (pH 2.8) deaerated citrate-phosphate buffers. In each case, the voltammetry was tested in both neutral and acidic solutions. Since the pK_a of the side chain on DA is 9 and that for DOPAC is 4.5, DA is cationic at both pH 7.4 and 2.8, whereas DOPAC is anionic at pH 7.4 and nonionic at pH 2.8.

Voltammetry of DA and DOPAC following electrochemical treatment in a deaerated pH 7.4 citrate-phosphate buffer solution is shown in Figure 1. Voltammograms are compared at pH 7.4 (Fig. 1A,1B) and at pH 2.8 (Fig. 1C,1D). At pH 7.4, voltammograms for DA become more Nernstian following anodic treatment, while those for DOPAC become less Nernstian. This charge selective electron transfer enhancement following treatment in pH 7.4 buffer is similar to what was shown previously by Saraceno and Ewing (37). However, voltammograms obtained in pH 2.8 solution are significantly different. Following anodic treatment, voltammograms of DA in pH 2.8 solution again become more Nernstian. In contrast to voltammograms for DOPAC at pH 7.4, voltammograms for DOPAC at pH 2.8 show little change after anodic treatment of the electrode. The average wave slopes for voltammograms obtained under these conditions are given in Table I.

These data suggest that DOPAC, which is nonionic at pH 2.8, has reduced electrostatic repulsive interactions with the electrode surface and allows for better charge transfer in comparison with its anionic form at pH 7.4. As a control, the average wave slopes were evaluated before and after treatment for 4-MC, which is a nonionic catechol and these wave slopes are also shown in Table I. This treatment was conducted in pH 7.4 buffer and the voltammetry at pH 2.8. Since 4-MC is nonionic, its voltammetry before and after anodic treatment should be similar to that for DOPAC at pH 2.8. Surprisingly, the wave slope for 4-MC becomes greater (31 mV) after treatment indicating slowed charge transfer kinetics. This data appears to indicate that the mechanism for oxidation of DOPAC following anodic treatment can not be explained by electrostatic arguments alone. However, in the case of electron transfer to DOPAC, the electrostatic interaction appears to play an important role.

In order to probe further the nature of the carbon surface, the effect of treating the electrode in an acidic buffer has been explored. Significant differences are observed when anodic treatment is conducted in pH 2.8 citrate-phosphate solution. Voltammograms for DA and DOPAC before and after treatment in pH 2.8 buffer are shown in Figure 2 and average wave slopes are given in Table II. In contrast to the previous treatment at pH 7.4, the voltammetry for both DA and DOPAC becomes less Nernstian, indicating "deactivation" of the surface. This decrease in reversibility is independent of the solution pH at which the voltammetry is carried out (tested at pH 2.8 and 7.4). Deactivation for both DA and DOPAC following anodic treatment is interesting since electrochemical anodic treatment has been shown to improve voltammetry at many different types of carbon electrodes including ultrasmall carbon ring electrodes (2,3,13-25,30,37). These data indicate that the pH of the solution in which anodic treatment occurs is an extremely important parameter in order to obtain an activated surface.

There have been several reports that suggest that anodic treatment acts to oxidize the surface of carbon electrodes and creates an oxide layer (13,18,28-31). Kepley and Bard have clearly shown the formation of a graphitic oxide layer following anodic treatment in acidic solution (28). This graphite oxide has been shown to have cation-exchange properties and can adsorb analyte (39,40). The data shown here strongly suggest that anodic treatment of carbon ring electrodes results in oxidation of the carbon ring surface and creates an amorphous graphite oxide layer similar to that reported by Kepley and Bard (28). This model is consistent with the present observations that the pH of the solutions for test voltammograms is important in determining the nature of the voltammetry after anodic treatment in pH 7.4 buffer for carbon ring electrodes. Also consistent with this model are test voltammograms that are highly dependent on the solution in which the anodic treatment occurs, where activation can occur following pH 7.4 treatment and deactivation occurs following pH 2.8 treatment. It is possible that anodic treatment leads to the growth of an oxide layer on the electrode surface, which is a weak cation exchanger and is, hence, affected by solution pH. This effect of solution pH during anodic treatment might be explained by an oxide layer that is less concentrated in ion exchange sites and, hence, serves mainly to block transport to the electrode surface. This model of the activated surface following treatment is also consistent with that proposed by Beilby and Carlsson (30).

Extensive anodic treatment in 3 M KOH. To further explore the characteristics of the hypothesized oxide formation on carbon ring electrodes, two protocols were developed for anodic treatment carried out at high pH. The first of these was oxidation of the electrode surface in 3 M KOH. Figure 3 shows voltammograms of DA and DOPAC before and after this extensive KOH treatment. Voltammograms following this treatment have two noticeable changes. First, a change in mass transport is apparent going from steady state sigmoidal voltammograms to peak shaped voltammograms. Second, the overall current response for both DA and DOPAC is attenuated. The lower current response immediately suggests an apparent reduction of the electrode surface area. This might be occurring from formation of a thick graphite oxide film on the surface and would be consistent with reports of Keply and Bard (28), Beilby and Carlsson (30) and others (13,14,18-20,31). The attenuated and peak shaped response is puzzling in that partial electrode blockage should still result in steady state voltammetry. It is possible that oxide layer formation results in the creation of a "thin layer cell" reservoir on the surface into which analyte can partition. However, diffusion into the film from the bulk of solution would need to be the rate limiting step to explain the depletion effect observed in the voltammograms. In this model, a [redacted] thin layer cell with a porous surface results which could explain the asymmetric voltammogram. Also, the overall current response is higher for DA vs DOPAC relative to the initial response of the limiting current for each case (peak current ratio ± standard error of the mean, DA/DOPAC = 2.9 ± .9) and strongly suggests that a partitioning effect is at least partially responsible for the observed voltammetry.

Soaking experiment. To qualitatively test the extent of adsorption of analyte into the hypothesized oxide layer, electrochemically treated electrodes soaked for 15 minutes in a 0.1 mM DA solution. This was followed by voltammetry in only pH

7.4 citrate-phosphate buffer. Voltammograms obtained following the soaking are shown in Figure 4. An attenuated peak current is observed at about 0.15 V and is indicative of adsorption on the electrode. This is consistent with data presented by Kovach et al. (30) following extensive anodic treatment of cylindrical carbon fiber electrodes.

Effect of scan rate. Figure 5 shows voltammograms obtained before and after extensive KOH treatment at scan rates of 100 mV/s and 5 mV/s. As in Figure 4, voltammograms obtained at 100 mV/s following treatment (Fig. 5B) are peak shaped and greatly attenuated. Computer simulations have been used (41) to predict the shape of voltammograms that result when adsorbed analyte dominates the current response with little or no contribution from analyte diffusing in from the bulk. This behavior results from non-ideal thin layer cell behavior with finite diffusion and is consistent with the peaked voltammetry shown here. At the slower scan rate of 5 mV/s (Fig. 5C), a steady state sigmoidal shaped voltammogram is observed. At the higher scan rate, the current is dominated by mass transport from a finite pool (the oxide layer) and results in peak shaped voltammetry. It is important to note (Fig. 5D) that a steady state component is evident which results in a limiting current after the peak which is identical to that observed at 5 mV/s (Fig. 5C).

Intermediate anodic treatment in 3 M KOH. There is some question as to whether the observed peak shaped voltammetry following anodic treatment in 3 M KOH results from simply breaking the seal between the carbon and the epoxy and, in effect, creating a thin layer cavity or "leaky electrode." To address this issue, effects from a less extensive anodic treatment in 3 M KOH were examined. This treatment was carried out by using a linear potential scan (400 mV/s) to 1.8 V vs SSCE, pausing for ~3 s instead of 15 s, then linearly scanning back to -0.2 V. Figure 6 shows voltammograms for DA before and after this treatment. Analogous to the previous treatment (pausing for 15 s), the voltammogram following treatment is peak shaped and attenuated. However, following 5 consecutive voltammograms of DA at this treated electrode, a steady state response for DA can again be obtained. This is in contrast to the voltammograms obtained after extensive anodic treatment (Figure 3) which remain peak shaped even up to 15 consecutive scans. These data again support the contention that the peak shaped voltammograms obtained following extensive anodic treatment do indeed result from formation of an inhibiting oxide layer. It appears that if this layer is formed from an "intermediate anodic treatment" then it is not stable and can be partially removed after consecutive voltammetric scans. Thus, it appears that the peak shaped voltammograms obtained following extensive anodic treatment are not due to cracks and fissures in the glass and epoxy structure surrounding the carbon electrode. Furthermore, a thin layer crevice would provide, if nothing else, additional current from oxidation of analyte inside the crevice, the exact opposite of the attenuated voltammograms shown here.

Minimized anodic treatment in KOH. A third procedure was carried out to perform anodic treatment of the surface of carbon ring electrodes in high pH solution. This procedure involved scanning the electrode potential at 400 mV/s from - 0.2 V to 1.8 V vs SSCE with immediate scan reversal at 1.8 V. This anodic pretreatment was performed in 0.3 and 0.003 M KOH solutions. Voltammograms of DA and DOPAC before and after this minimized oxidation are shown in Figure 7. Anodic treatment in 0.3 M KOH results in more Nernstian voltammograms for DA with a slight attenuation of the limiting current. The same treatment results in voltammograms for DOPAC that are also more Nernstian, but in the case of DOPAC about a 50% reduction in the limiting current occurs. However, electrodes treated in 0.003 M KOH provide voltammograms for DOPAC that are more Nernstian with only a slight reduction in the limiting current. Simple speculation leads to the suggestion that the mass transport of DOPAC is more easily blocked after anodic treatment than is DA. In addition, mass transport of DA might also be facilitated by ion exchange into an oxide surface layer. Sujaritvanichpong and Aoki (19) have shown that considerable adsorption of DOPAC occurs following anodic treatment of carbon fiber electrodes and three different voltammetric responses can result. Table III shows the average wave slopes before and after minimized treatment in KOH, with voltammetry conducted in both pH 7.4 and pH 2.8 solutions. The wave slopes after treatment are more Nernstian for DA at both 2.8 and pH 7.4. However, the wave slopes for voltammograms of DOPAC after KOH treatment are more Nernstian in pH 7.4 solution and show little change (statistically) in pH 2.8. Again, an electrostatic effect appears to be important in the charge transfer of DOPAC after anodic treatment of carbon ring electrodes. Thus, treatment in KOH under these conditions appears to form a non-homogeneous oxide layer which does not appear to inhibit the rate of electron transfer (as evidenced by the wave slopes), but appears to attenuate in the current response, with a larger effect on the mass transport of the anionic DOPAC relative to cationic DA.

Model of carbon ring electrode surface. The data presented here lead to a speculative mechanism for oxidation of catechols at ultrasmall carbon ring electrodes following anodic electrochemical treatment. The basic premise is that enhancements of the electron transfer rate following treatment are a function of the surface cleanliness and the orientation of the carbon structure (7,8,10,18,21,25-27). Thus, anodic activation might function in two ways: first, it can serve to clean and expose new sites of carbon which have predominantly edge plane orientation; second, it can result in the formation a graphite oxide layer which has a structure that is dependent on the pH of the treatment solution. The growth of this oxide layer may start from underneath the surface and in the process of growth and expansion, break the carbon surface lattice and expose new carbon with edge plane orientation. Apparently, it is a combination of both the carbon edge plane orientation and oxide layer which contribute to the voltammetry shown in this work.

Kepley and Bard have described this oxide layer as a "porous, swollen, and hydrated layer" composed of microscopic particles (28). Using STM, Gewirth and Bard have studied the formation of this oxide layer after anodic treatment and found that the oxide layer grows as islands on the surface, exposing some areas and covering other regions (29). This suggests that electrochemical treatment forms a non-uniform oxide layer with areas or sites of freshly exposed carbon planes. The end result might be described as an oxide surface with pin holes. Graphite oxide has been reported to have cation-exchange properties (39,40). Accordingly, at carbon ring electrodes treated in pH 7.4 buffer, the oxide layer formed can favorably partition cations and block anions from reaching the electrode surface. In the case of extensive KOH treatment, the amorphous oxide film is thick and prevents effective diffusion to the surface which results in the observation of an attenuated current response. The mechanism of mass transport leading to the peak shaped voltammograms is still not clearly understood, but a "thin layer-like" effect is apparent. Minimized oxidation in KOH results in first cleaning the surface and changing the carbon structure, then forming islands of gossamer film thereby exposing activated sites on the electrode surface. Because the surface film is thin, only minimal blocking occurs (more so with DOPAC than DA) and transport into the film is not the rate limiting step, thus sigmoidal voltammetry results. Finally, the treatment in low concentrations of KOH does not result in significant preferential enhancement of the apparent charge transfer rate (electron exchange and mass transport effects combined) for cationic DA relative to anionic DOPAC.

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TABLE I
Comparison of Average Wave Slopes Following Anodic Treatment

Solution pH	Wave Slope for Cleaved Electrode (mV/decade)[a]	Wave Slope for Treated Electrode (mV/decade)[a]	Change in Waveslope (mV/decade)	n
		Treatment in pH 7.4		
		(DA)		
7.4	139 ± 2	119 ± 10	-20	11
2.8	92 ± 8	38 ± 5	-54	6
		(DOPAC)[b]		
7.4	161 ± 20	197 ± 13	36	9
2.8	81 ± 4	83 ± 10	2	7
		(4-MC)		
2.8	84 ± 3	115 ± 7	31	7

[a] Error values are standard error of the mean

[b] Data from voltammograms of DOPAC at treated electrodes with a reduction in the limiting current of greater than 40% were not included: 0% of all electrodes examined at pH 7.4; 36% at pH 2.8.

TABLE II
Comparison of Average Wave Slopes Following Anodic Treatment

Solution pH	Waveslope for cleaved Electrode (mV/decade)[a]	Wave Slope for Treated Electrode (mV/decade)[a]	Change in Waveslope (mV/decade)	n
		Treatment in pH 2.8		
		(DA)		
7.4	144 ± 11	166 ± 5	22	7
2.8	94 ± 5	140 ± 8	46	4
		(DOPAC)		
7.4	141 ± 5	180 ± 23	39	5
2.8	87 ± 2	113 ± 6	26	8

[a] Error values are standard error of the mean

Table III
Comparison of Average Wave Slopes Following Anodic Treatment in KOH

Solution pH	Wave Slope for Cleaved Electrode (mV/decade)[a]	Wave Slope for Treated Electrode (mV/decade)[a]	Change in Wave Slope (mV/decade)	n
		(DA)		
pH 7.4	98 ± 9	36 ± 1	-62	6
pH 2.8	76 ± 2	49 ± 8	-27	4
		(DOPAC)		
pH 7.4	119 ± 6	55 ± 7	-64	8
pH 2.8	75	85	10	2

[a] Error values are standard error of the mean

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FIGURE LEGENDS

Figure 1: Oxidation of 0.1 mM DA (A,C) and DOPAC (B,D) at carbon ring electrodes (1-10 μm). Top: Cyclic voltammetry at pH 7.4 and (bottom) at pH 2.8 before (——————) and after (---------) anodic treatment in pH 7.4 buffer. Scan rate: 100 mV/s.

Figure 2: Oxidation of 0.1 mM DA (A,C) and DOPAC (B,D) at carbon ring electrodes. Top: Cyclic voltammetry at pH 7.4 and (bottom) at pH 2.8 before (——————) and after (---------) anodic treatment in pH 2.8 buffer. Scan rate: 100 mV/s.

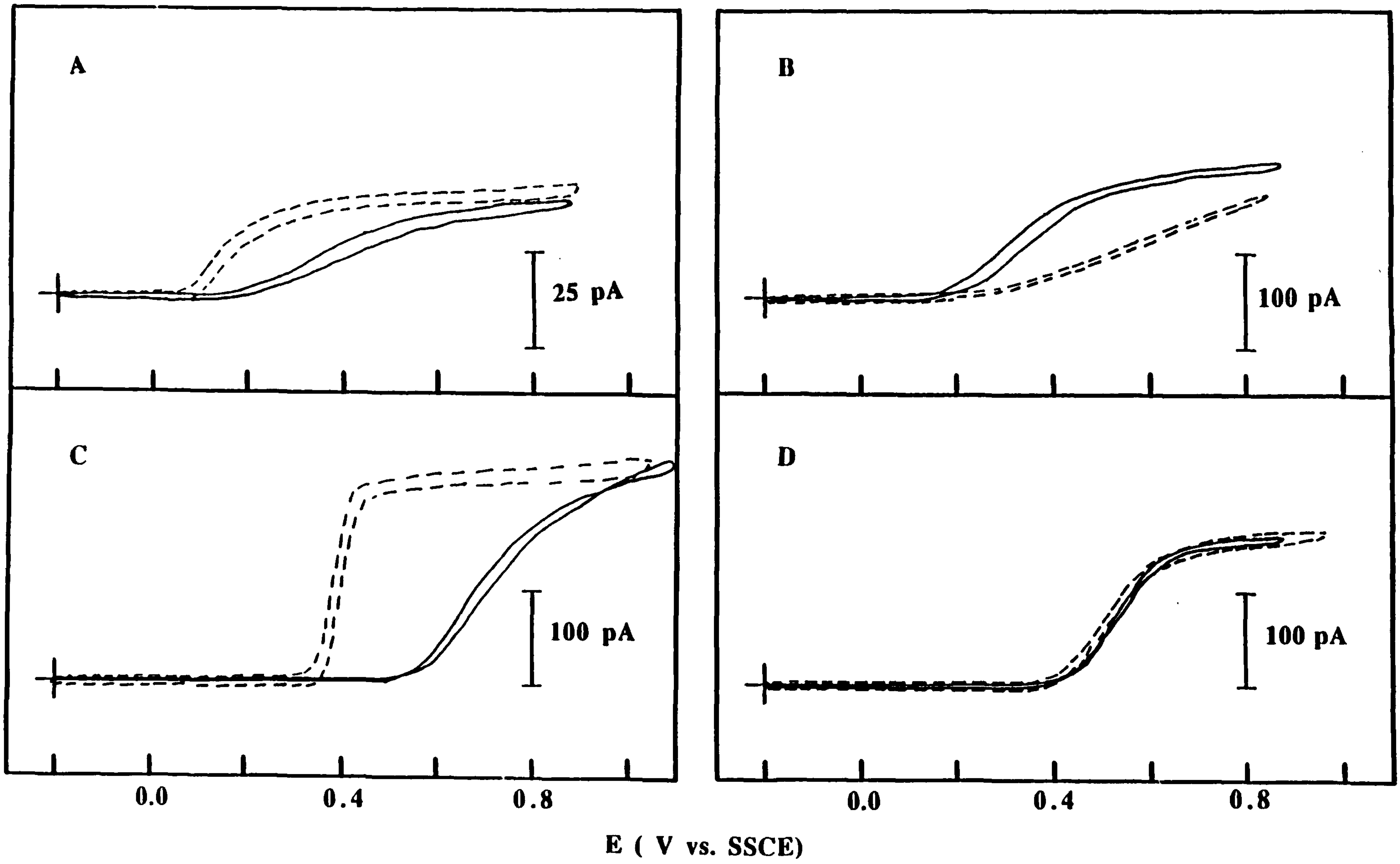
Figure 3: Top: Oxidation of 0.1 mM DA (A) and DOPAC (B) at freshly cleaved carbon ring electrodes. Bottom: Oxidation of 0.1 mM DA (C) and DOPAC (D) after extensive anodic treatment in 3 M KOH. Treatment consisted of cycling (@ 200 mV/s) up to 1.8 V, pausing for 15 seconds, then cycling back. Scan rate: 100 mV/s. Voltammograms were carried out in pH 7.4 citrate-phosphate buffer.

Figure 4: Oxidation of 0.1 mM DA at a freshly cleaved carbon ring electrode (A) and after extensive anodic treatment in 3 M KOH (B) (Conditions for anodic treatment are the same as for Fig. 3). (C): Cyclic voltammetry in straight citrate-phosphate buffer (pH 7.4) after soaking in 0.1 mM DA solution for 15 minutes. Scan rate: 100 mV/s. Voltammograms were carried out in pH 7.4 citrate-phosphate buffer.

Figure 5: Oxidation of 0.1 mM DA at 100 mV/s at freshly cleaved carbon ring electrode (A) and after extensive anodic treatment in 3 M KOH (B) (Conditions for anodic treatment are the same as in Fig. 3). Oxidation of 0.1 mM DA at 5 mV/s (C) and 100 mV/s (D) after extensive treatment. Voltammograms were carried out in pH 2.8 citrate-phosphate buffer.

Figure 6: Oxidation of 0.1 mM DA at freshly cleaved electrode (A) and after intermediate anodic treatment in 3 M KOH (B). The Treatment consisted of cycling (@ 200 mV/s) up to 1.8 V, pausing for 3 seconds, then cycling back. (C): Oxidation of 0.1 mM DA obtained after 5 voltammetric consecutive scans at the treated electrode. Scan rate: 100 mV/s. Voltammograms were carried out in pH 7.4 citrate-phosphate buffer.

Figure 7: Oxidation of 0.1 mM DA (A) and DOPAC (B) at carbon ring elctrodes before (————) and after (----------) minimal anodic treatment in 0.3 M KOH and oxidation of DOPAC (C) before and after same treatment in 0.003 M KOH. Treatment consisted of one 400 mV/s cycle between -200 mV and 1.8 V without pausing. Scan rate: 100 mV/s. Voltammograms were carried out in pH 7.4 citrate-phosphate buffer.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B
100 pA
C
100 pA
D
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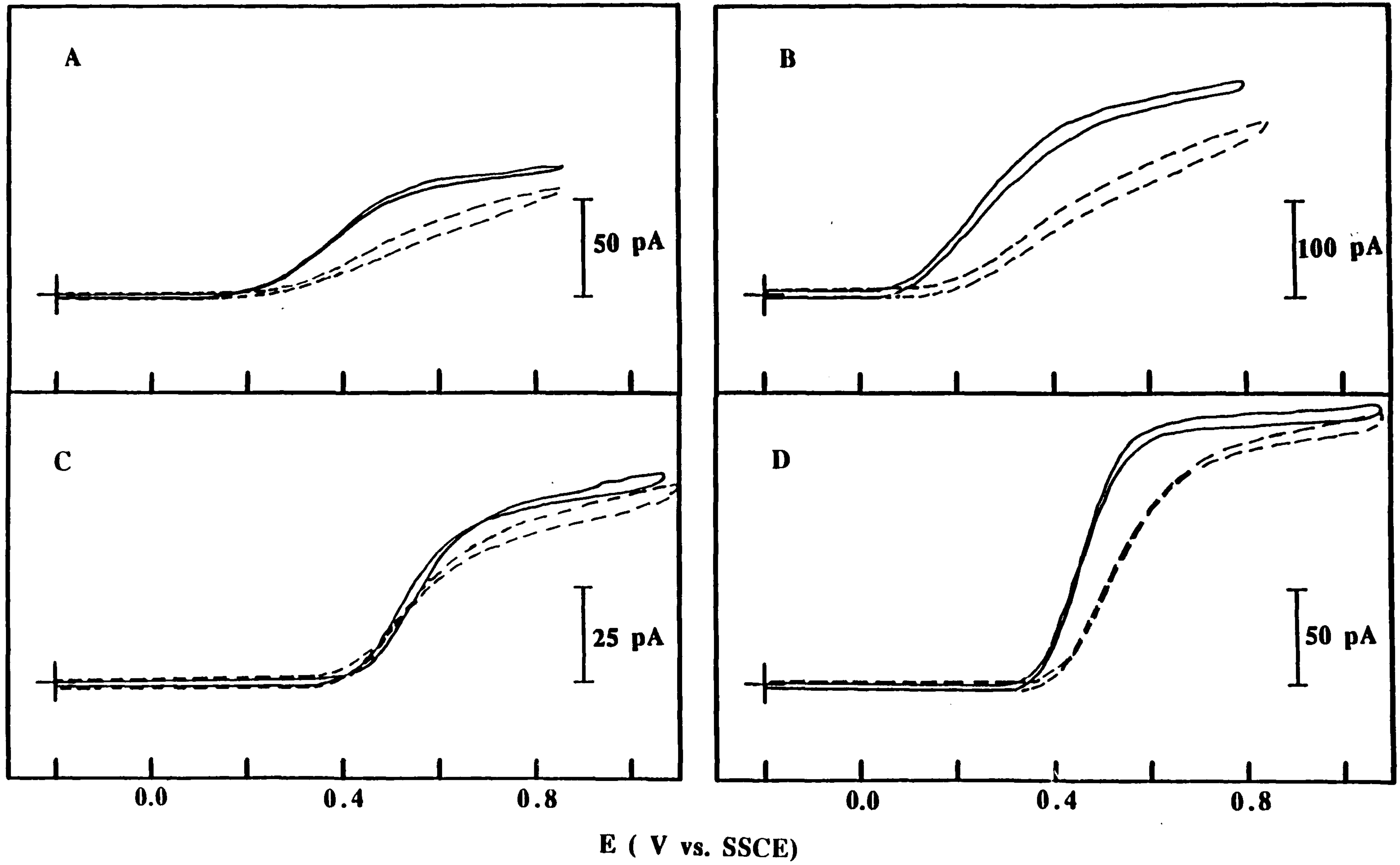
0.4
0.8
0.0
0.4
0.8
E (V vs. SSCE)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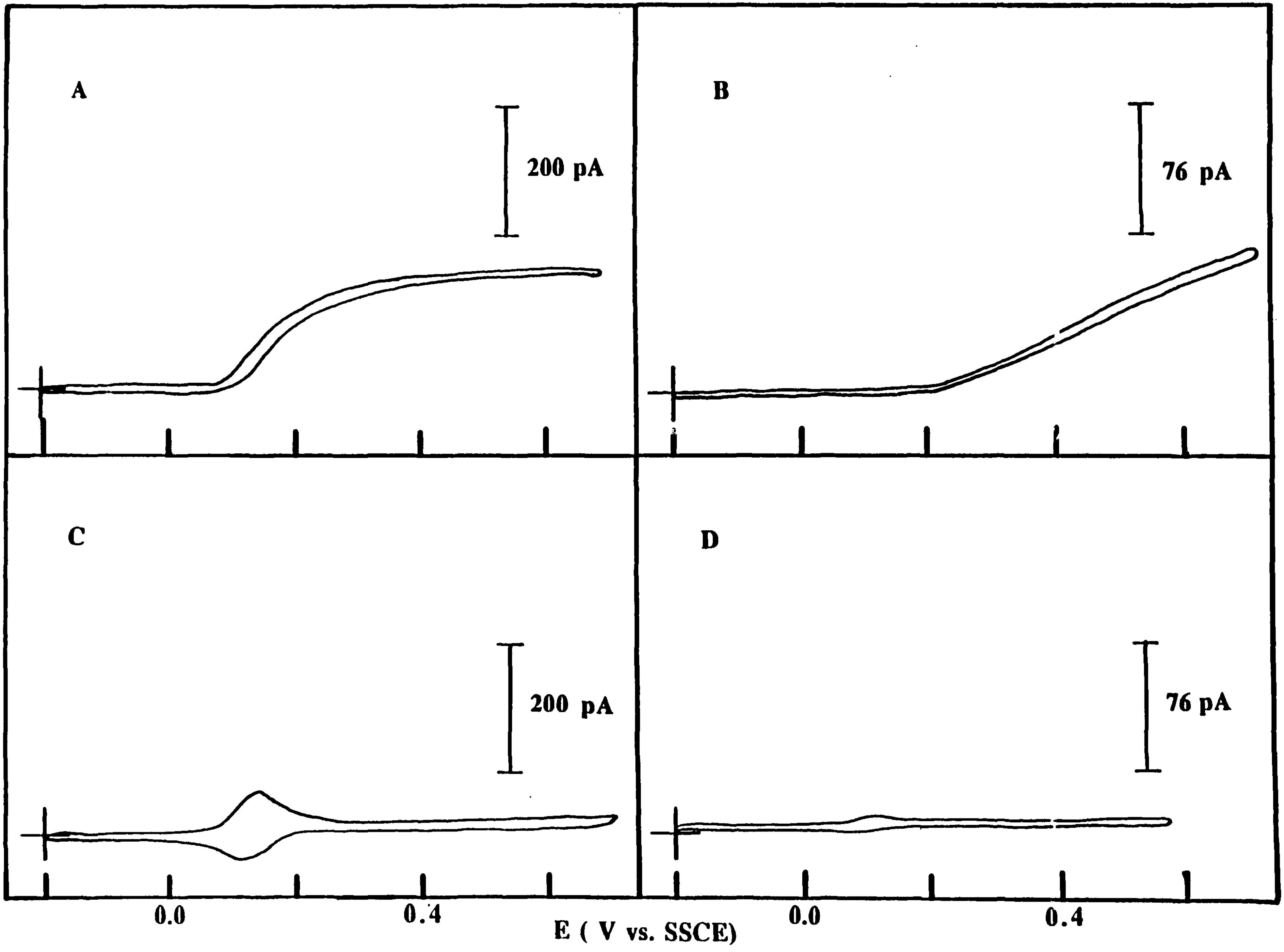
E (V vs. SSCE)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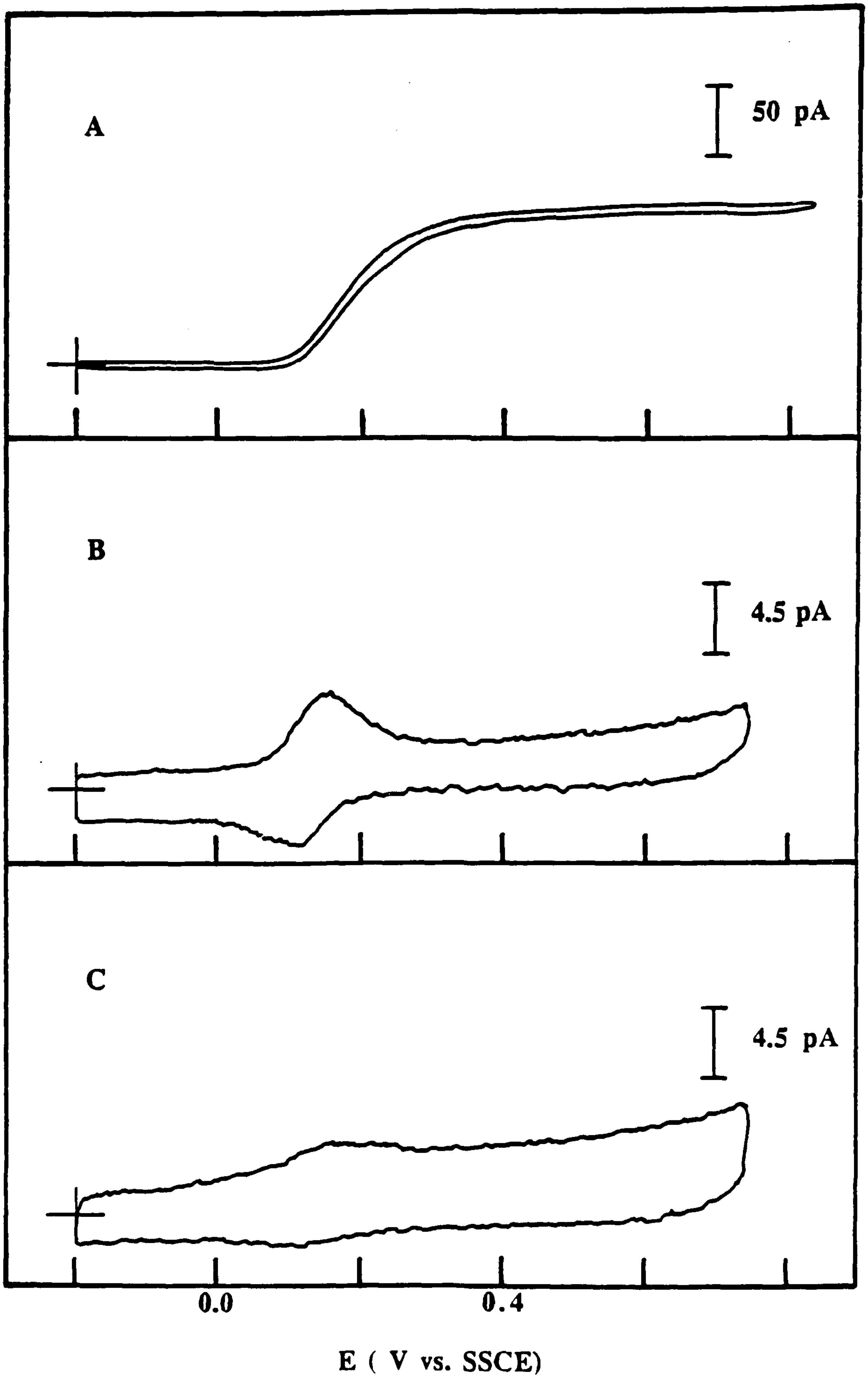
E (V vs. SSCE)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C
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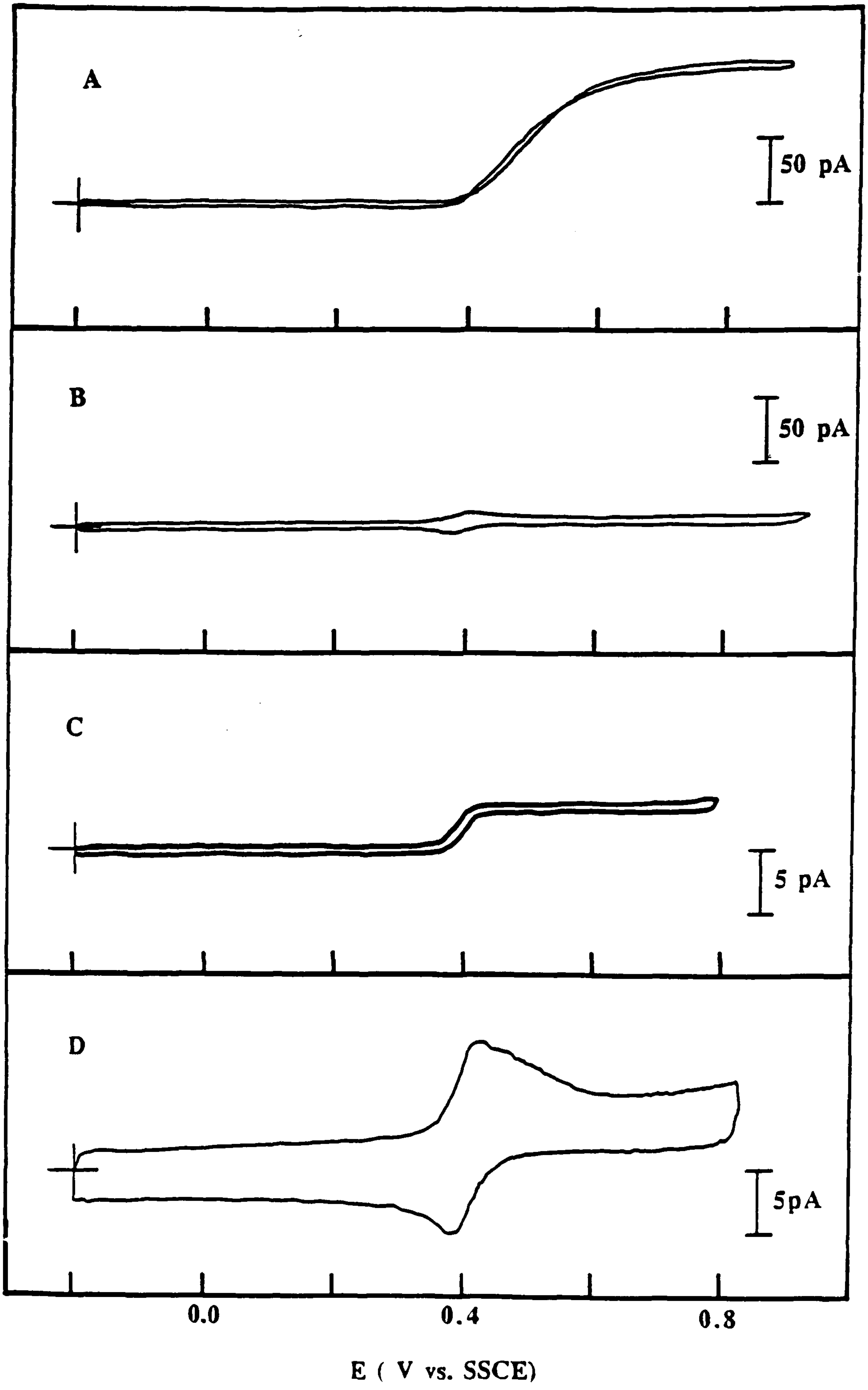
0.4
E (V vs. SSCE)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B
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C
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D
5pA
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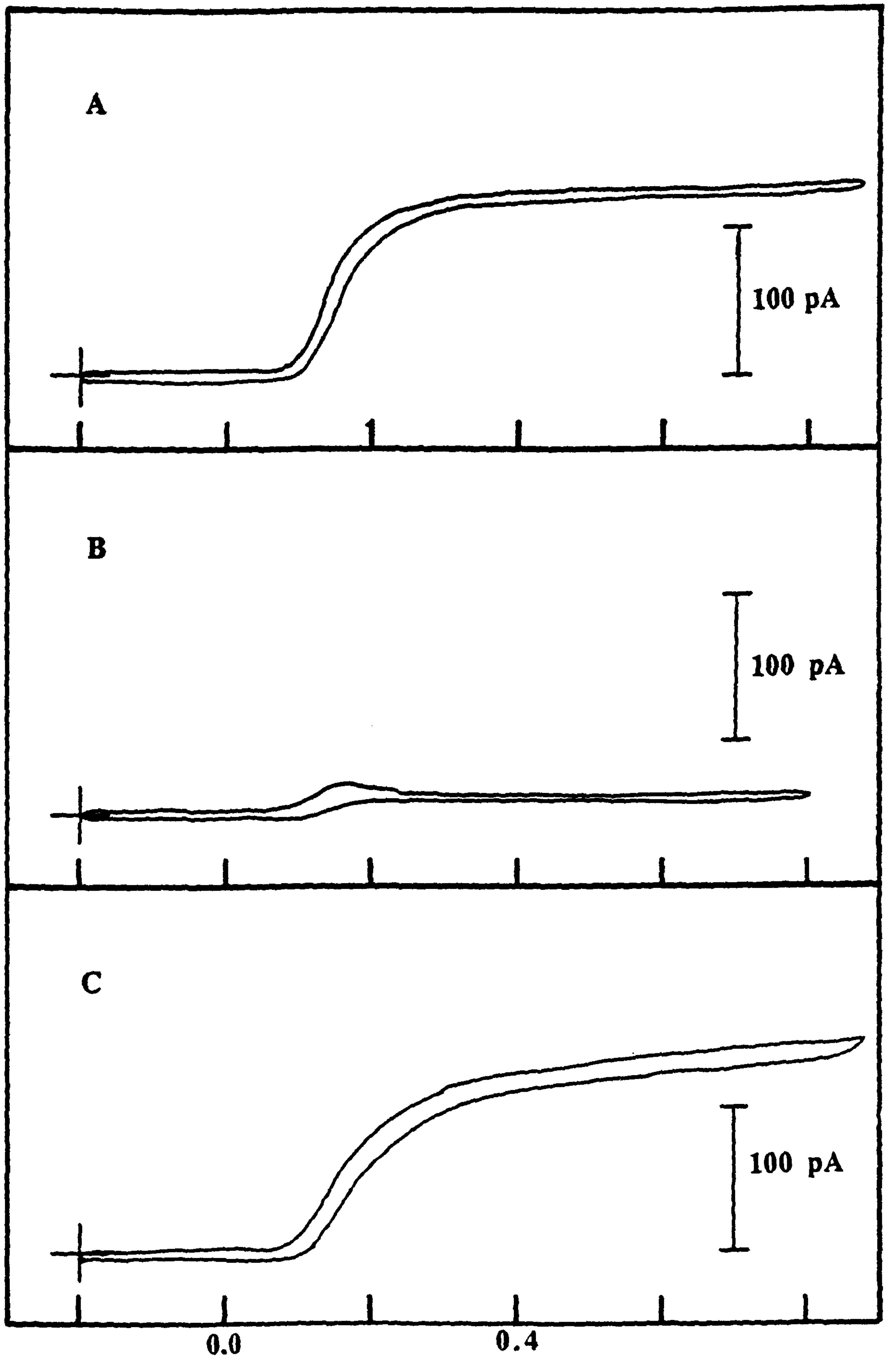
0.4
0.8
E (V vs. SSCE)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B
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C
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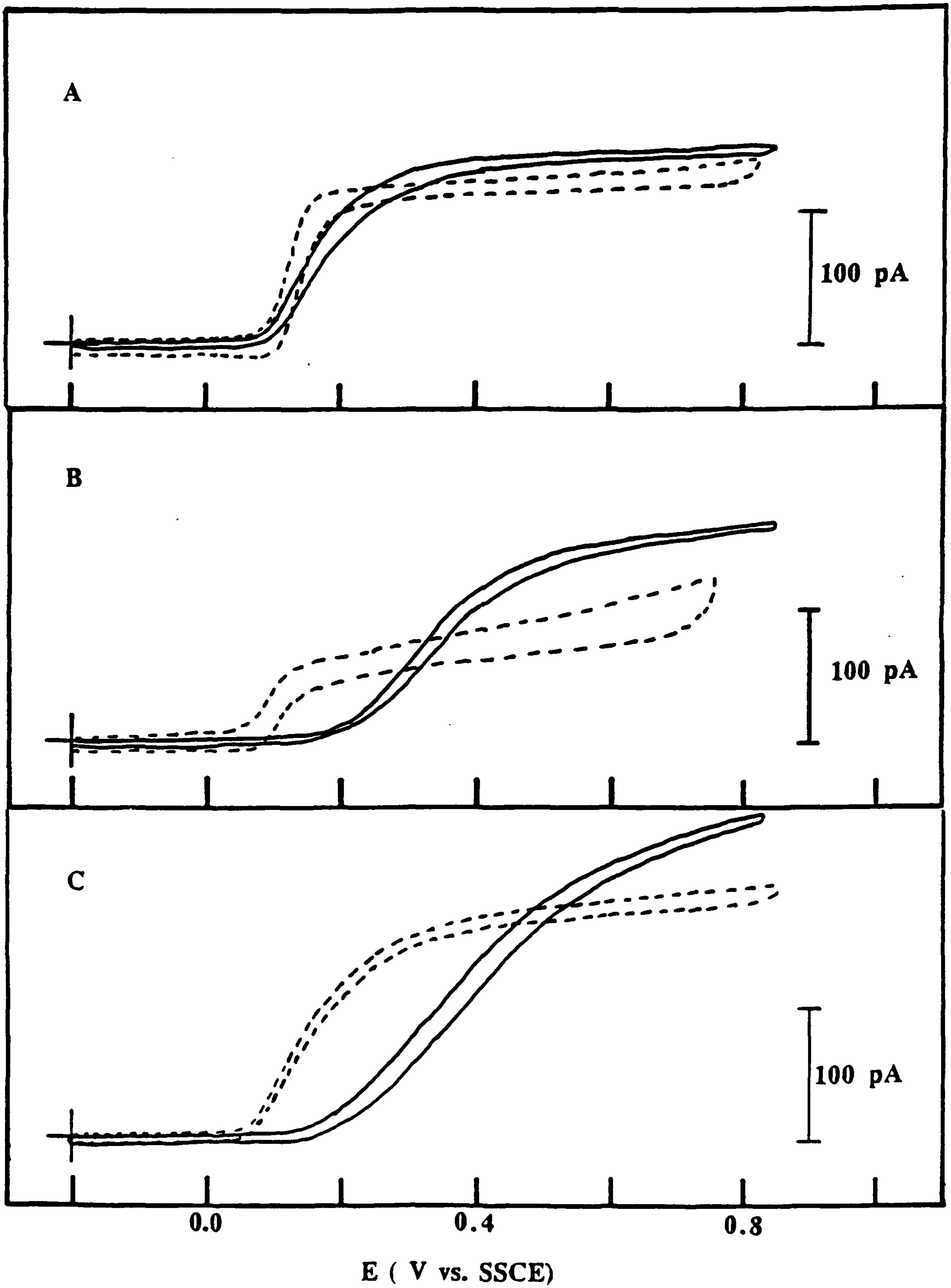
E (V vs. SSCE)


A
100 pA
B
100 pA
C
100 pA
0.0
0.4
0.8
E (V vs. SSCE)