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Electrocatalysis of anodic oxygen-transfer reactions: alpha-lead dioxide electrodeposited on stainless steel substrates

J. FENG

Department of Chemistry, Guangzhou Normal College, Guangzhou, Guangdong, People's Republic of China

D. C. JOHNSON*

Department of Chemistry and Ames Laboratory, Iowa State University, Ames, IA 50011, USA

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Dense and uniform films of alpha-PbO_2 were electrodeposited on the surfaces of various types of stainless steel. In strongly alkaline media, these films were found to be very stable and exhibited significant electrocatalytic activity for the oxidation of Cr(III) and CN^-. In acidic media, alpha-PbO_2 films deposited on type-416 stainless steel, which had been passivated by anodization in a phosphate solution, were relatively stable and exhibited catalytic activity for oxidation of Mn^{2+}. Rate constants for the anodic oxygen-transfer reactions of Cr(III), CN^- and Mn(II) were estimated from data obtained at rotated disk electrodes.

1. Introduction

Electrolytically deposited PbO_2 can exist in two polymorphic forms. The beta-form, deposited from acidic solutions of Pb(II), has a slightly distorted rutile structure. The alpha-form, deposited from neutral and slightly alkaline solutions, has the columbite form [1, 2]. Deposition of alpha-PbO_2 from 2 M NaOH saturated with PbO(s) has also been described [3].

Electrodes consisting of films of both alpha-PbO_2 and beta-PbO_2 formed by electrodeposition on inert substrates have been applied successfully for numerous anodic electrosynthetic reactions [2, 4]. Noble metal substrates, while receiving much attention in the laboratory, are too expensive to be practical as substrates for PbO_2-film electrodes of large area intended for industrial applications. Alternately, more economical materials receiving attention have included Pb, Pb alloys, graphite, Ti, and plastics [5–10]. Matantsev [11] tested Ni, Al, Cr, Fe, Armoiron^R, ferrosilicon, and stainless steel, and concluded that these materials are not appropriate as substrates.

Research to improve the performance of lead–acid batteries has considered the effects of metal impurities (for example, Ag, As, Co, Mn, Ni, Se, Sn, Te, V and Ti) on structure, oxygen stoichiometry, crystal morphology and self-discharge rates [12]. Recently, films of Bi-doped beta-PbO_2 electrodeposited on Au and Pt rotating disk electrodes (RDEs) were demonstrated to have increased electrocatalytic activity for several anodic oxygen-transfer reactions, as compared to pure beta-PbO_2 films on the same substrates [13]. We also have preliminary data indicating that PbO_2 films doped with Fe(III) exhibit a moderately increased activity for oxidation of several compounds [14].

Research summarised here was based on the premise that iron and/or stainless steels (SS) can be useful as inexpensive substrates for pure and modified PbO_2-film electrodes. The manufacture of passive 'iron-black' films (Fe_3O_4), and phosphate-containing films on Fe and Fe-alloys, has become a mature technology [15] and these coatings can protect the substrates during exposure to highly corrosive conditions. It is well known, for example, that iron tanks are used successfully for storage and shipment of concentrated nitric and sulphuric acids. The corrosion resistance of stainless steels (SS) is provided by very thin surface films of passive oxides which are self-healing in a wide variety of corrosive environments. It has been reported [15] that SS can be highly resistant to 50% boiling caustic soda and some austenitic steels can withstand strong acid. Furthermore, PbO_2 films might offer additional protection to SS substrates because of their stability in strongly acidic and alkaline media. These facts inspired us to test various passivated SS substrates for use in the preparation of PbO_2-film anodes.

Passive oxide films can be formed at the surfaces of Fe and Fe-alloys. Furthermore, passive phosphate-containing films can be formed anodically in phosphate media. Beneficial modification of the electrodeposited films was expected to result from incorporation of one or more of the components of the stainless steels into the deposited PbO_2 films (i.e., Fe). Two basic questions pervaded this research: (i) Can PbO_2 films on stainless steel substrates function satisfactorily at large positive values of applied potential in various aqueous

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* Author to whom correspondence should be addressed.

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media? (ii) Do these electrodes exhibit improved catalytic activity for O-transfer reactions in comparison with pure PbO_2 films on noble metal substrates?

2. Experimental details

2.1. *Reagents*

All chemicals were AR Grade from Fisher Scientific, Alfa Products, or Aldrich Chemicals. Water was purified in a NANOpure II system (SYBRON/Barnstead). Supporting electrolytes were 1.0 M $HClO_4$, 0.50 M H_2SO_4, 0.014 M $NaHCO_3$/0.011 M Na_2CO_3 (pH 10.0), 0.30 M HOAc/0.50 M NaOAc (pH 5.0) and 2.0 M NaOH. Anodic passivation of SS surfaces was performed in 1 M Na_3PO_4/4 M H_3PO_4 (pH 0.7). Other reagents included $Cr(NO_3) \cdot 9H_2O$, NaCN, and $Mn(NO_3)_2$.

2.2. *Instrumentation*

Noble metal disk electrodes included Au (0.196 cm^2) and Pt (0.159 cm^2) (Pine Instrument Co.). Stainless steel (SS) disks were constructed from the SS alloys 416 (0.196 cm^2), and 302, 304, 317, and 321 (0.349 cm^2) (Fry Steel Co.). Disk electrodes were mounted in a Model MSR Rotator (Pine Instrument Co.). Exhaustive electrolysis was performed at films deposited on cylindrical electrodes made from Pt-screen and 304-SS screen (Johnson-Matthey).

Electronic instrumentation included a Model RDE4 potentiostat (Pine Instrument Co.), a Model 551 potentiostat (ECO, Inc.), a Model 7035B X-Y recorder (Hewlett Packard), a Series 5500 stripchart recorder (Houston Instruments Co.), a model IV current source (E. H. Sargent and Co.), a Research Coulometer (U.K. Thompson Electrochem Ltd), a Zeromatic SS-3 pH meter (Beckman Co.), and a Model 197 digital multimeter (Keithley Instruments).

2.3. *Procedures*

The surfaces of SS disk electrodes were polished with 320-grit Carbimet paper strips followed by 1 μm diamond paste. Some SS substrates were passivated by anodic polarization (5 min at -192 mA) in the phosphate solution described previously. Dissolution of components of the SS surfaces was initially very rapid, as indicated by a slow initial rate for O_2 bubble formation. Passivation increased, as noted by the increased rate of O_2 formation, until reaching an apparent steady-state value after 3–4 min. The resulting electrode surfaces had a uniformly dark gray appearance.

In some cases, thin Au films were anodically deposited at constant current on SS substrates (1.0 mA cm^{-2} for 20 min) from solutions containing 4.0 mg ml^{-1} $HAuCl_4 \cdot 3H_2O$, 6.4 mg ml^{-1} KCN and 4.0 mg ml^{-1} $NaHPO_4 \cdot 7H_2O$. Alpha-PbO_2 films were deposited anodically for 3.0 min at 0.35–0.40 V from 2.0 M NaOH saturated with PbO(s). Bismuth-doped beta-PbO_2 films were deposited anodically at + 1.60 V for 20 min from solutions containing 1.0 mM Pb(II) plus 0.70 mM Bi(III) in 1.0 M $HClO_4$.

Positive and negative scan limits in voltammetric studies were chosen on the basis of onset of anodic evolution of O_2 and cathodic dissolution of the oxide films, respectively. All potentials were recorded and are reported as volts measured with respect to a saturated calomel electrode (V versus SCE).

2.4. *Electrocatalytic comparisons*

To facilitate intercomparison of the electrocatalytic activities of various electrodes, apparent heterogeneous rate constants (k_{app}, cm s^{-1}) were estimated from plots of the reciprocal of the anodic current (i), normalized for area (A) and bulk concentration of reactant (C^b), according to Equation 1. In Equation 1, J is the

$$\frac{1}{J} = \frac{1}{i/AC^b} = \frac{1}{nFk_{app}} + \frac{3.091}{0.62 n_{eff} FD^{2/3} v^{1/6}} \left[\frac{1}{W^{1/2}} \right] \tag{1}$$

normalized current density (mA mM^{-1} cm^{-2}), n_{eff} is the effective number of electrons in the reaction (eq mol^{-1}), v is the solution kinematic viscosity (cm^2 s^{-1}), W is the rotation speed (rev min^{-1}), 3.091 is the constant for interconversion of the square roots of W and rotational velocity (rad s^{-1}), and F and D have their conventional electrochemical significance. The value of n_{eff} for kinetically coupled reactions can be smaller than the total number (n_{tot}) of electrons determined by exhaustive electrolysis. Values of electrode current (i) were measured at a constant applied electrode potential and were corrected for the background.

3. Results and discussion

3.1. *Deposition of alpha-PbO_2 films*

Several types of stainless steels were considered as substrates for anodic deposition of alpha-PbO_2. Members of the 300-series contain high levels of Cr and Ni, and are called 'austenitic' stainless steels. These are considered to have high corrosion resistance. Members of the 400-series have a high iron content and have good mechanical properties, but with some sacrifice in corrosion resistance.

The voltammetric responses (i–E) for several bright (i.e., untreated) and passivated stainless steel (SS) rotated disk electrodes (RDEs) were obtained in 2.0 M NaOH after saturation with Pb(II) by addition of excess PbO(s) powder. The data are typified by i–E curves shown in Fig. 1. The background response obtained for the absence of PbO(s) (dashed lines) contains peaks and waves which are attributed to anodic dissolution of components in the SS substrates, as well as anodic formation and cathodic dissolution of surface oxide. It is obvious that the overpotential for O_2 evolution is larger at SS surfaces which had been anodically passivated (e.g., Curves A and C)

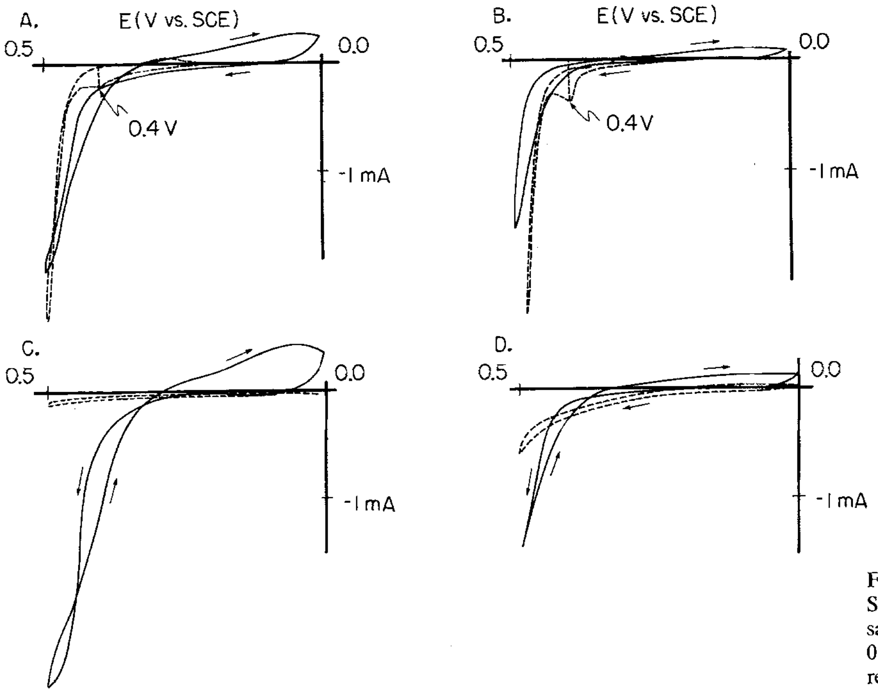

Fig. 1. Voltammetric response of various SS rotated disk electrodes in PbO(s)-saturated 2.0 M NaOH. Conditions: 0.6 V min^{-1}, 1600 rev min^{-1}. Curves: (- - -) response, (——) PbO(s)-saturate d solution.

in comparison to the bright surfaces (e.g., Curves B and D). With PbO(s) present (solid lines), significantly larger anodic currents were observed near +0.4 V which correspond to the anodic deposition of alpha-PbO_2. The broad cathodic waves observed at approximately 0.0 V on the negative potential scan result from cathodic dissolution of PbO_2 deposited during the previous positive scan (see especially Curve C). The anodic currents for the deposition process are significantly less than the mass transport limited value and, therefore, are probably proportional to the true surface area. Accordingly, the deposition current is significantly larger at SS surfaces which have been passivated, because this anodic process results in a significant increase in surface roughness (see Curve C for 416-SS).

The colours of the deposited oxide films were observed to differ significantly on the various substrates. The film was green on bright 321-SS, yellow on 302-SS, brown on 304-SS and purple on 416-SS. Whereas differences in colour intensity are expected to be the result of variations in film thickness, differences in hue are interpreted to result from differences in oxide composition and/or structure. We conclude tentatively that alpha-PbO_2 was formed by the anodic deposition from the highly alkaline media and that Fe(III) stripped from the SS substrate simultaneously with the deposition process was present as a doping agent in the PbO_2 film.

A strongly adherent PbO_2 film is highly desirable for industrial applications. A simple test for film adherence was applied. A piece of conventional, transparent adhesive tape (Scotch, 3M) was pressed onto the deposited films and then removed by a swift pull. No alpha-PbO_2 was observed to be removed from the films deposited on passivated 416-SS substrates. The same test applied to alpha-PbO_2 films on Au and Au-plated SS substrates resulted in obvious removal of small portions of PbO_2.

3.2. *Corrosion resistance of alpha-PbO_2 films*

The resistance to anodic corrosion of electrodes consisting of alpha-PbO_2 films on 304- and 416-SS substrates was tested by determination of the weight loss which occurred during a 24 h period of anodic polarization under galvanostatic conditions in solutions of 0.10 M Cr(III) in 2.0 M NaOH and 1.0 M H_2SO_4. The results, summarised in Table 1, indicate that the electrodes tested can withstand anodic polarization in alkaline media with virtually no loss of mass. In acidic media, the electrodes experienced considerable weight loss over a 24 h period. This loss is concluded to have occurred primarily by dissolution of the substrate in regions exposed to the electrolyte solution through small pinholes or fissures in the alpha-PbO_2 films.

Table 1. Weight loss of anodes during 24 h of galvanic polarization in alkaline and acidic media

Media[a]	*Anode*	*Initial Weight (g)*	*Final Weight (g)*	*Weight Change (mg)*
0.10 M Cr(III) in 1.0 M NaOH	alpha-PbO_2 on 304-SS	46.5315	46.5310	−0.5
	alpha-PbO_2 on 416-SS[b]	42.3209	42.3208	−0.1
0.10 M Cr(III) in 1.0 M H_2SO_4	Bi-PbO_2 on Au	46.4288	46.4256	−3.2
	alpha-PbO_2 on 416-SS[b]	42.3397	42.3110	−28.7
	Bi-PbO_2 on 416-SS[b]	50.2062	50.2022	−4.0

[a] Current density: 0.050 A cm^{-2}.

[b] SS substrate passivated by anodic treatment in phosphate solution.

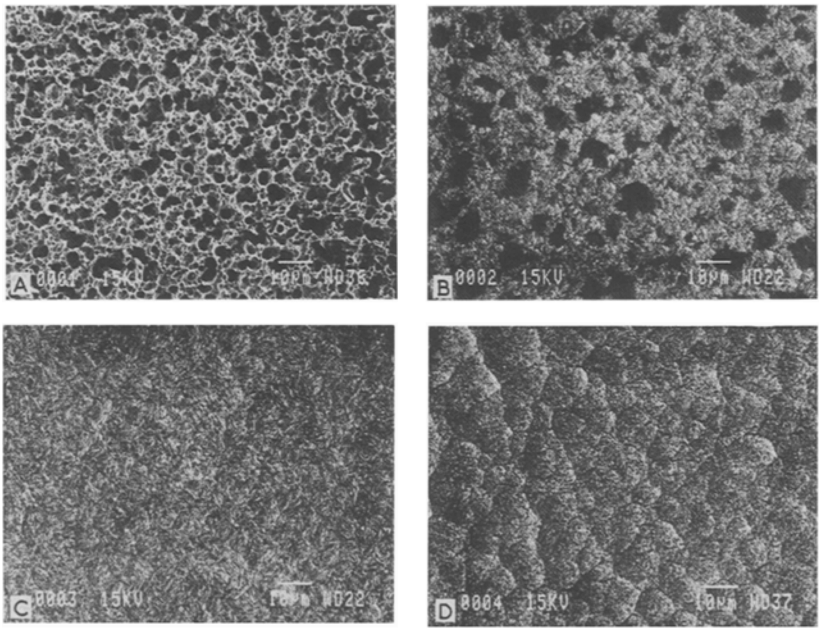

Fig. 2. Micrographs of substrates and PbO_2 films. (A) Passivated 416-SS, (B) alpha-PbO_2 on Au, (C) alpha-PbO_2 on bright 416-SS, (D) alpha-PbO_2 on passivated 416-SS.

3.3. *Scanning Electron Microscopy*

Micrographs obtained by Scanning Electron Microscopy (SEM) are shown in Fig. 2 for passivated 416-SS, and for alpha-PbO_2 films on Au and on passivated and bright 416-SS. The surface morphology of the films is similar, although tiny holes are apparent in the film on the Au substrate. We conclude, on the basis of Fig. 2, that the alpha-PbO_2 films on SS substrates were more dense, uniform and relatively free of holes and fissures. Furthermore, since both alpha- and beta-PbO_2 films exhibited excellent stability in acidic media, we conclude that the continuous, hole-free films of PbO_2 can contribute to increased corrosion resistance of SS substrates.

3.4. *Anodic oxidation of Cr(III)*

The electrolytic oxidation of Cr(III) is of major importance in a wide range of electrochemical applications [11, 16, 17] and PbO_2 has been considered widely as a practical anode material in those processes. The usual conditions for Cr(III) oxidation are highly corrosive because of both the high acidity and the large anodic

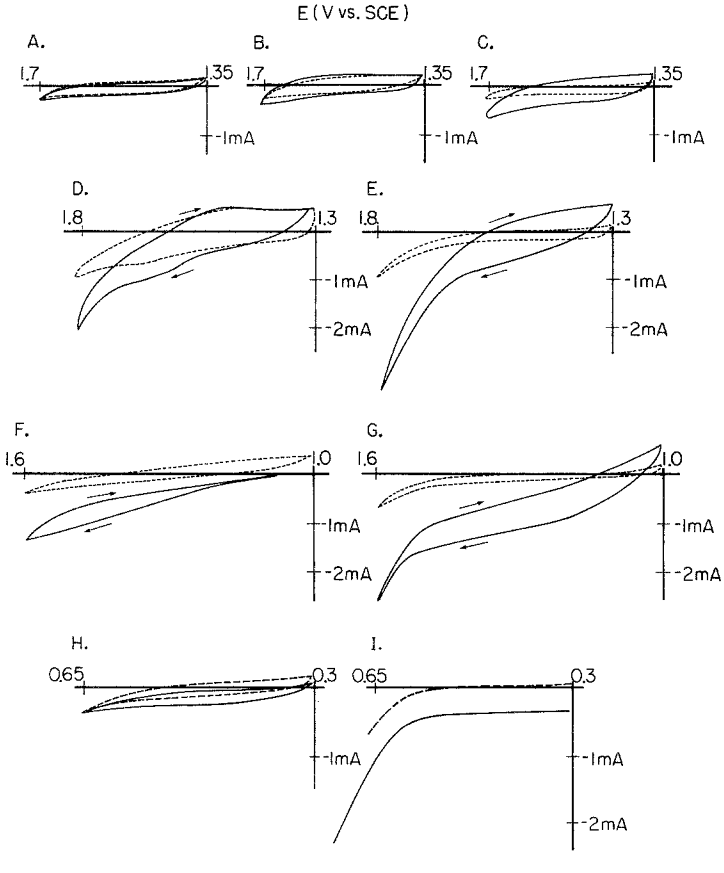

Fig. 3. Voltammetric response for Cr(III) at a rotated disk electrode. Conditions: 0.60 V min^{-1}, 1600 rev min^{-1}. Curves: (– – –) residual response, (——) response for Cr(III). Solutions: (A–C) 1.0 mM Cr(III)/0.50 M H_2SO_4, (D–E) 5.0 mM Cr(III/0.50 M Na_2SO_4 (pH 2.3), (F–G) 1.0 mM Cr(III)/1.0 M HOAc/NaOAc (5.0), (H–I) 1.0 mM Cr(III)/2.0 M NaOH. Electrodes: (A) alpha-PbO_2 on Pt, (B, D, F, H) Bi-doped beta-PbO_2 on Au, (C, E, G, I) alpha-PbO_2 on passivated 416-SS.

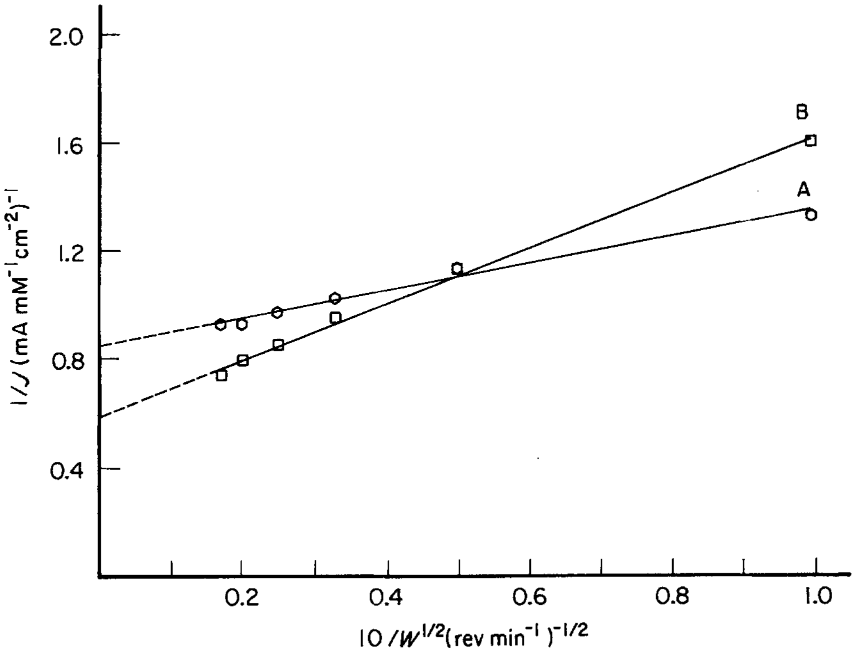

Fig. 4. Plots of $1/J$ versus $1/W^{1/2}$ for oxidation of 5.0 mM Cr(III) at 1.6 V in 0.50 M Na_2SO_4 (pH 2.3). Electrodes: (A) Bi-doped beta-PbO_2 on Au, (B) alpha-PbO_2 on passivated 416-SS.

potential required. The anodic evolution of O_2 always is observed to occur simultaneously with Cr(III) oxidation and this side reaction decreases the current efficiency for the desired process. It is highly desirable to identify anode materials which have high stability and which can selectively catalyse the oxidation of Cr(III) without a significant increase in the rate of O_2 evolution.

Voltammetric curves shown in Fig. 3 provide the basis for estimating the catalytic activities of the various alpha-PbO_2 film electrodes for oxidation of Cr(III). It is readily apparent that the residual response for the alpha-PbO_2 films on SS is virtually the same as for this film on noble metals in the range of potential values tested (compare dashed lines in Curves A and C). However, this evidence is only a tentative indicator of long term stability of the PbO_2-substrate interface.

As anticipated on the basis of balanced half reaction for conversion of Cr(III) to Cr(VI), the activity of electrodes for Cr(III) oxidation is sensitive to changes in solution pH. There was virtually no anodic reaction of Cr(III) for the electrodes in highly acidic media (Curves A–C), and only slight reactivity at pH 2.3 (Curves D and E) and pH 5.0 (Curves F and G). In

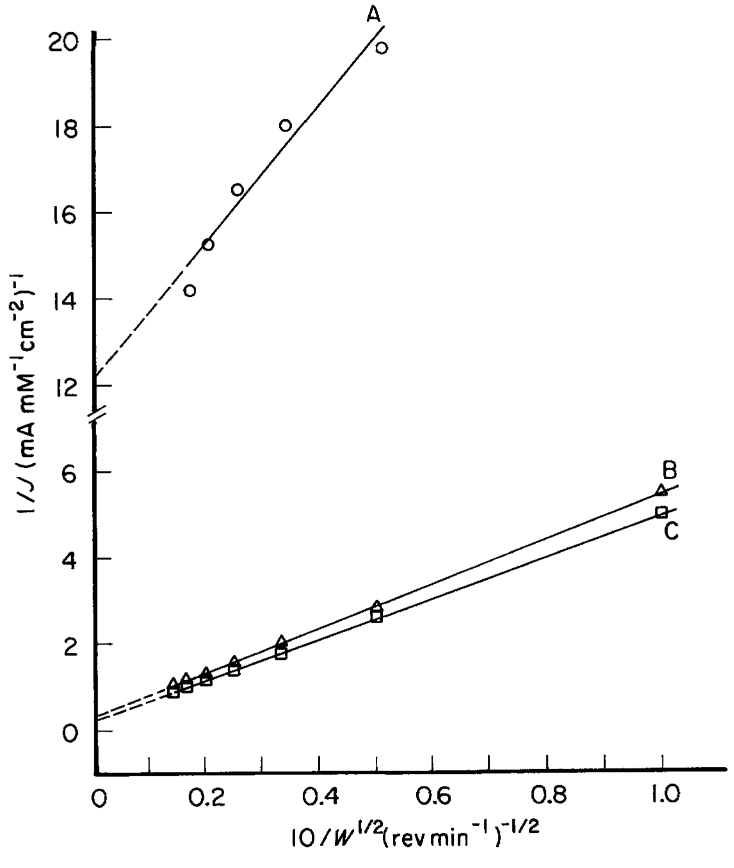

Fig. 5. Plots of $1/J$ versus $1/W^{1/2}$ for oxidation of 5.0 mM Cr(III) at 1.4 V in 1.0 M HOAc/NaOAc (pH 5.0). Electrodes: (A) alpha-PbO_2 on Pt, (B) Bi-doped beta-PbO_2 on Au, (C) alpha-PbO_2 on passivated 416-SS.

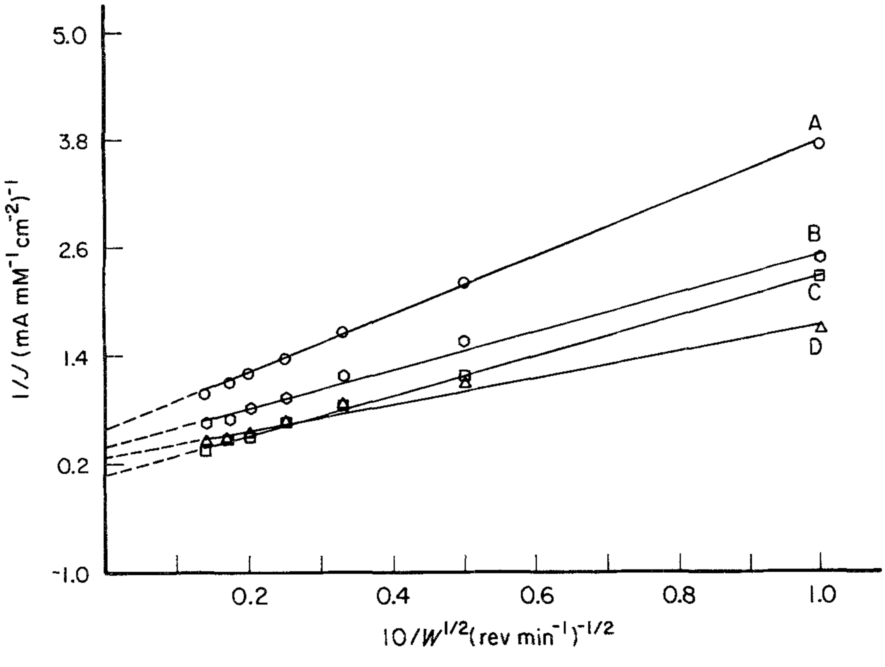

Fig. 6. Plots of $1/J$ versus $1/W^{1/2}$ for oxidation of 5.0 mM Cr(III) at 0.50 V in 2.0 M NaOH. Electrodes: (A) Bi-doped beta-PbO_2 on Au, (B) alpha-PbO_2 on Pt, (C) alpha-PbO_2 on bright 416-SS, (D) alpha-PbO_2 on passivated 416-SS.

2.0 M NaOH, the oxidation of Cr(III) occurred at the alpha-PbO_2 film on the SS electrode (Curve I) to yield a current plateau over an extended potential range (+ 0.3 to + 0.6 V), whereas little activity was observed for Bi-doped beta-PbO_2 on Au (Curve H) or alpha-PbO_2 on Pt (data not shown).

The catalytic activities of the various deposited films for Cr(III) oxidation were compared based on rate constants estimated from the intercepts of plots of $1/J$ versus $1/W^{1/2}$ (see Equation 1). Since the intercept of a $1/J$–$1/W^{1/2}$ plot is related to the reciprocal of the apparent rate constant (k_{app}), these plots provide easy visual comparison of the catalytic activities of the various electrodes. The plots of experimental data are shown in Figs 4 to 6 for three different pH values, and the kinetic results are summarised in Table 2. It is apparent from Table 2 that the alpha-PbO_2 films on SS substrates exhibited the highest catalytic activity for oxidation of Cr(III) in 2.0 M NaOH. Furthermore, activity was greatest for the case of bright rather than passivated 416-SS with the reaction being virtually mass transport controlled (i.e., $1/nFk_{app} = 0$). Pure alpha-PbO_2 films on Pt exhibited moderate activity in the strongly alkaline media but very low activity in acidic media. The activity of Bi-doped beta-PbO_2 films on Au was very low. The higher activity for alpha-PbO_2 films on SS is concluded to be the result of incorporation into the oxide of Fe(III) which was produced by anodic dissolution of the SS substrate simultaneously with the deposition process. Since the anodic passivation of SS in the phosphate solution protects the SS substrate from anodic dissolution during the subsequent electrodeposition of PbO_2, the electrodes comprised of alpha-PbO_2 films on passivated SS were more stable but less active than the films on the untreated bright SS surfaces. It is speculated that deposition of alpha-PbO_2 from a solution containing Fe(II and/or III) will produce an anode with optimum stability and reactivity. Further testing of this assumption will be presented later [14].

Values of $n_{tot} = 3.0 \pm 0.2\,\mathrm{eq\,mol^{-1}}$ for Cr(III) were determined by exhaustive electrocatalysis at cylindrical-screen SS and Pt electrodes which had been plated with alpha-PbO_2 films (see Table 2) and the product was concluded to be Cr(VI).

Table 2. *Rate constants for oxidation of Cr(III)*

Anodes	*Media*	n^{b}_{tot} *(eq mol^{-1})*	$10^3 k_{app}$ *(cm s^{-1})*
alpha-PbO_2 on bright 416-SS	2 M NaOH	3.0 ± 0.02	97 ± 1
	HOAc/NaOAc (pH 5.0)	3.0 ± 0.09	19 ± 1
	0.5 M Na_2SO_4 (pH 2.3)	NA[c]	
	0.5 M H_2SO_4	NA[c]	
alpha-PbO_2 on 416-SS after passivation	2 M NaOH	3.0 ± 0.07	67 ± 1
	HOAc/NaOAc (pH 5.0)	3.0 ± 0.1	38 ± 1
	0.5 M Na_2SO_4 (pH 2.3)	3.0 ± 0.05	46 ± 1
	0.5 M H_2SO_4	NA[c]	
Bi-doped beta-PbO_2 on Au	2 M NaOH	3.0 ± 0.03	59 ± 1
	HOAc/NaOAc (pH 5.0)	3.0 ± 0.3	13 ± 2
	0.5 M Na_2SO_4 (pH 2.3)	3.0 ± 0.2	33 ± 1
	0.5 M H_2SO_4	NA[c]	
alpha-PbO_2 on Pt	2 M NaOH	3.0 ± 0.2	11 ± 1
	HOAc/NaOAc (pH 5.0)	3.0 ± 0.2	30 ± 1
	0.5 M Na_2SO_4 (pH 2.3)	NA[c]	
	0.5 M H_2SO_4	NA[c]	

[a] Experimental conditions for kinetic measurements are same as described for Figures 4A-C.

[b] Value of n_{tot} determined by controlled-potential exhaustive electrolysis.

[c] No activity observed.

3.5. *Anodic oxidation of cyanide*

The fast and efficient electrolytic degradation of CN^- by direct anodic reaction could have environmental significance for clean-up of wastes from metal plating

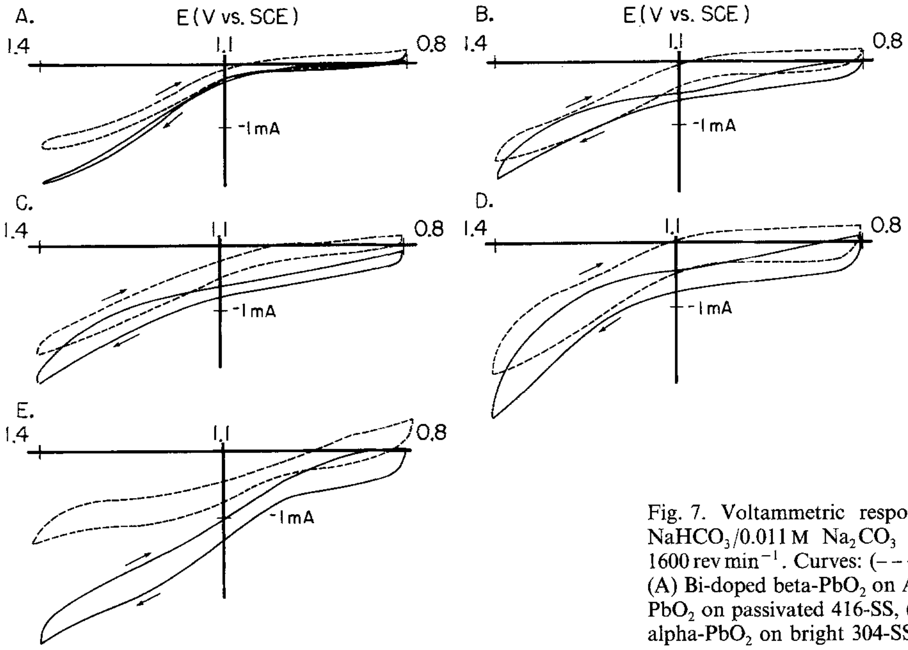

Fig. 7. Voltammetric response for 5.0 mM NaCN in 0.014 M $NaHCO_3$/0.011 M Na_2CO_3 (pH 10.0). Conditions: 0.6 V min^{-1}, 1600 rev min^{-1}. Curves: (- - -) residual, (——) NaCN. Electrodes: (A) Bi-doped beta-PbO_2 on Au, (B) alpha-PbO_2 on Au, (C) alpha-PbO_2 on passivated 416-SS, (D) alpha-PbO_2 on bright 416-SS, (E) alpha-PbO_2 on bright 304-SS.

industries [18, 19]. It is preferable that this degradation process be applied in alkaline media to minimize the volatility of HCN. Hence, alpha-PbO_2 films electrodeposited on SS substrates could be significant because of their electrochemical stability, provided they exhibit sufficient electrocatalytic activity for the desired oxygen-transfer reaction.

The voltammetric response of CN^- is compared in Fig. 7 for various electrodes in alkaline solutions. It is evident that the catalytic activity of the alpha-PbO_2 films on SS substrates was greater than that of the beta-PbO_2 film on Au. The greatest activity was for the bright 304-SS substrate (Curve E) and incorporation of Fe(III) into the alpha-PbO_2 films during deposition is concluded tentatively to have been responsible for the high electrocatalytic reactivity. The available potential range for CN^- oxidation was quite extensive, approximately +0.8 to +1.1 V versus SCE. For $E > +1.1$ V, evolution of O_2 occurred simultaneously with CN^- oxidation. As observed for Cr(III) oxidation, the PbO_2 films on the bright SS substrates exhibited higher catalytic activity but lower stability than for the passivated SS substrates.

The large activity of the alpha-PbO_2 film on the 304-SS substrate for oxidation of CN^- is readily apparent from plots of $1/J$ versus $1/W^{1/2}$ shown in Fig. 8. Values of k_{app} calculated from the intercepts are 0.020 cm s^{-1} at alpha-PbO_2 on 304-SS and 0.0063 cm s^{-1} at alpha-PbO_2 on passivated 416-SS. Only very small anodic signals were obtained for CN^- at alpha-PbO_2 on Au and Bi-doped beta-PbO_2 on Au, which is indicative of low catalytic activity. Furthermore, these anodic signals did not change with variation of the rotatation velocity, which is further support of the conclusion of kinetic control. The oxidation of CN^- in alkaline media was determined by exhaustive electrolysis to

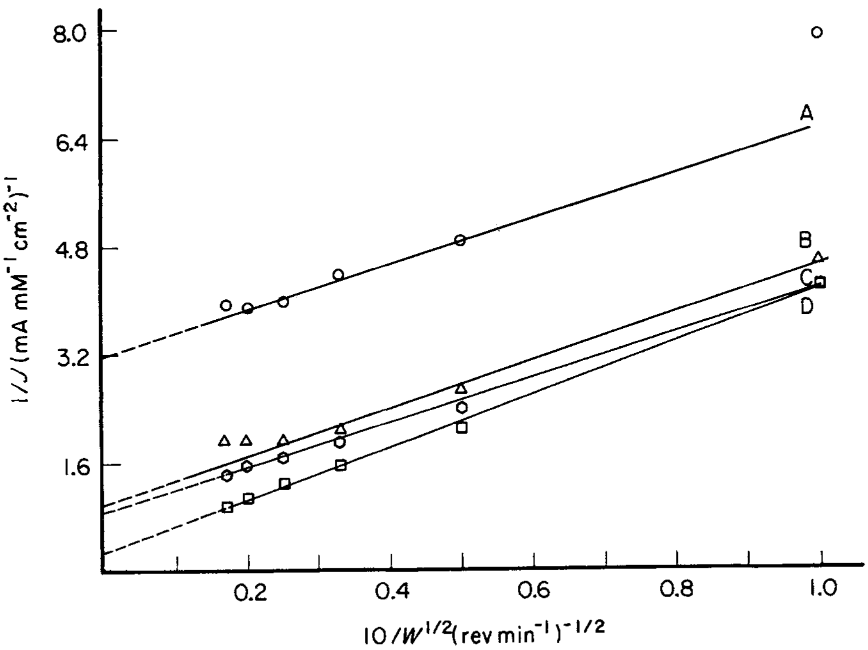

Fig. 8. Plots of $1/J$ versus $1/W^{1/2}$ for oxidation of 5.0 mM NaCN at 1.10 V in 0.014 M $NaHCO_3$/0.011 M Na_2CO_3 (pH 10.0). Electrodes: (A) Bi-doped beta-PbO_2 on Au, (B) alpha-PbO_2 on Au, (C) alpha-PbO_2 on passivated 416-SS, (D) alpha-PbO_2 bright 304-SS.

occur with $n_{tot} = 2.0 \pm 0.1\,\mathrm{eq\,mol^{-1}}$ at alpha-PbO_2 films deposited on the cylindrical Pt and 304-SS screen electrodes. We conclude the anodic reaction produces cyanate, as shown by Equation 2.

$$CN^- + 2OH^- \longrightarrow CNO^- + H_2O + 2e \quad (2)$$

Catalytic activity for CN^- oxidation was investigated for alpha-PbO_2 on bright 304-SS as a function of variation in the film thickness, deposition potential and solution pH. The maximum anodic response was obtained for a 30 min deposition. On the basis of the measured deposition current (-2.0 mA), $n_{tot} = 2.0\,\mathrm{eq\,mol^{-1}}$ and the density of alpha-PbO_2 ($9.38\,\mathrm{g\,cm^{-3}}$), we estimate the film thickness to be 30 μm for the optimum film. The catalytic activity was only a slight function of the deposition potential. For $E_{dep} = +0.35$ V, a higher activity was obtained than for $E_{dep} \gg 0.35$ V. We conclude that 0.35 V corresponds to the maximum rate of Fe(III) production at the 304-SS electrode during film deposition. Oxidation of CNO^-a to CO_2 is favoured thermodynamically at extremely high pH, as indicated by Equation 3. However, only a small increase in anodic current was observed at 0.85 V for a pH change from 9.5 to 10.6 and we conclude that CNO^- is the product of CN^- oxidation under these conditions.

$$2CNO^- + 8OH^- \longrightarrow 2CO_3^{2-} + N_2 + 4H_2O + 6e \quad (3)$$

3.6. *Anodic Oxidation of Mn(II)*

The catalytic activity of the various electrode surfaces for anodic oxidation of Mn(II) in 1.0 M $HClO_4$ was of interest because of the large number of oxygen atoms assumed to be transferred in the conversion to MnO_4^-. Furthermore, the rate for Mn(II) oxidation is slow at pure PbO_2 films deposited at noble-metal substrates. The Bi-doped beta-PbO_2 on Au has been determined to have a high catalytic activity for the reaction and the anodic signals are limited virtually by mass transport of the Mn(II). The voltammetric response of Mn(II) is summarised in Fig. 9 for Mn(II) in 1.0 M $HClO_4$. The background current at the alpha-PbO_2 film on the passivated 416-SS substrate is comparable to that for PbO_2 on the noble metal substrates. Without the passive coating formed during the phosphate treatment, the PbO_2 films failed to protect the SS substrates and rapid dissolution of the SS occurred with ultimate detachment of the PbO_2 films. Type-416 SS was very inert after anodic passivation in phosphate media and the roughened surface produced by

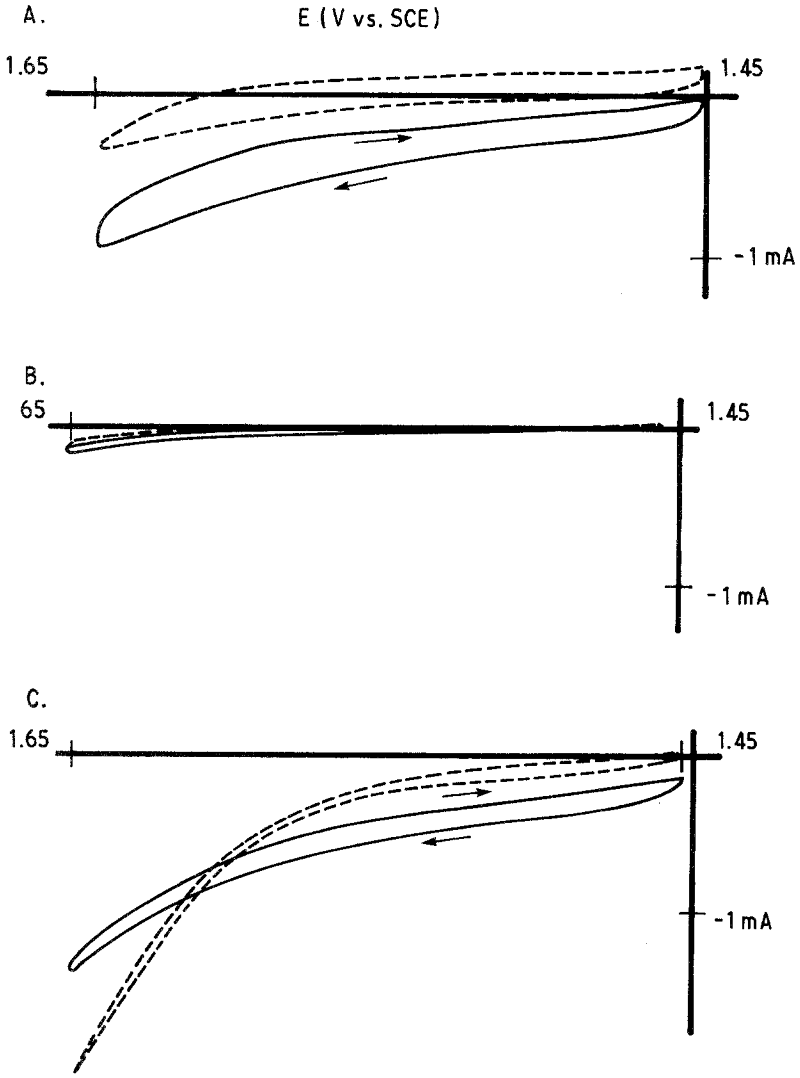

Fig. 9. Voltammetric response for 1.0 mM Mn(II) in 1.0 M $HClO_4$. Conditions: $0.60\,\mathrm{V\,min^{-1}}$, $1600\,\mathrm{rev\,min^{-1}}$. Curves: (– – –) residual, (——) Mn(II). Electrodes: (A) Bi-doped beta-PbO_2 on Au, (B) alpha-PbO_2 on Au, (C) alpha-PbO_2 on passivated 416-SS.

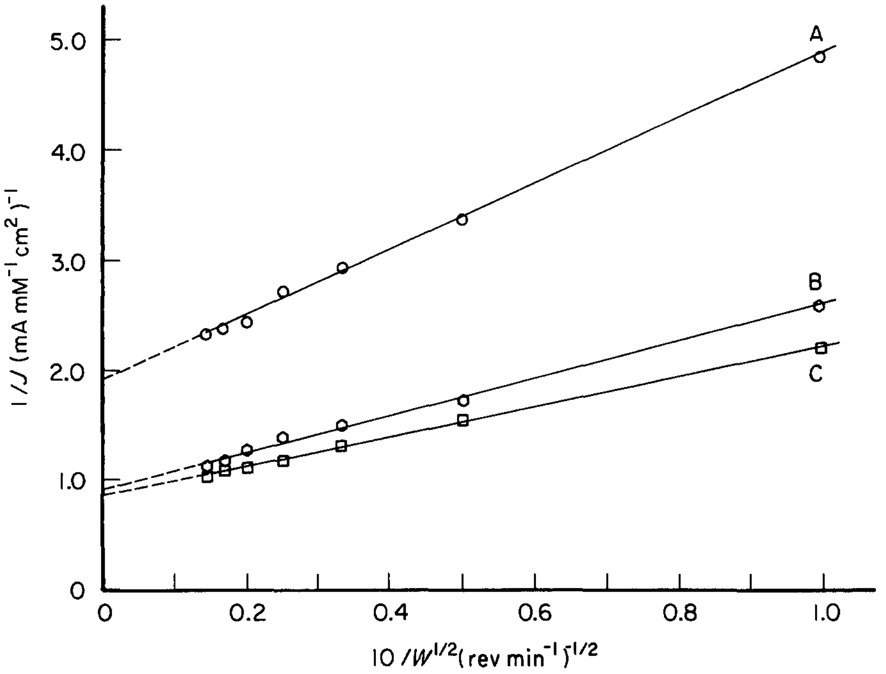

Fig. 10. Plot of $1/J$ versus $1/W^{1/2}$ for oxidation of 1.0 mM Mn(II) at 1.45 V in 1.0 M $HClO_4$. Electrodes: (A) Bi-doped beta-PbO_2 on Au, (B) alpha-PbO_2 on passivated 416-SS, (C) alpha-PbO_2 on Au-coated, passivated 416-SS.

the anodic process (see Fig. 2A) allowed for a strong attachment of the alpha-PbO_2 films. There was no evidence of removal of any portion of the deposited film onto a piece of transparent tape pressed against the film and then pulled away.

As was the observation for oxidation of Cr(III) and CN^-, catalytic activity for Mn(II) oxidation is greater for alpha-PbO_2 on SS rather than noble-metal substrates. Quantitative information to support this conclusion is shown in Fig. 10 as plots of $1/J$ versus $1/W^{1/2}$. The rate constants determined from the intercepts of the plots were 0.0011 cm s^{-1} at the Bi-doped PbO_2 film on Au, 0.0022 cm s^{-1} at the alpha-PbO_2 on a Au-coated 416-SS, and 0.0024 cm s^{-1} at the alpha-PbO_2 film on 416-SS. There was no advantage in using a Au inter-layer on the SS substrate either for higher catalytic activity or greater adherence of alpha-PbO_2 films.

4. Conclusions

A passive and roughened surface is produced on 416-SS by anodization in phosphate medium. The passivating layer is concluded to be conductive and the roughened surface allows for the strong adherence of electrodeposited alpha-PbO_2 films. Anodes consisting of alpha-PbO_2 on passivated 416-SS can be used in alkaline, neutral and slightly acidic media at large positive applied potential values without apparent decomposition.

Amperometric data support the conclusion that alpha-PbO_2 films on SS possess greater activity than observed for pure alpha-PbO_2 and Bi-doped beta-PbO_2 films on Au for the anodic O-transfer reactions of CN^- and Cr(III) in alkaline media, Cr(III) at pH $\geqslant$ 5, and Mn(II) in acidic media. The high catalytic activity is concluded tentatively to be the result of Fe(III), produced by anodic corrosion of the SS substrate simultaneously with deposition, which is incorporated into the PbO_2 films. We speculate that Fe(II and/or III) added to solutions of Pb(II) used for deposition of PbO_2 films will result in a significant increase in catalytic activity for the doped films.

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