

An electrochemical study of the composition of thin, compact Pd oxide films

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An electrochemical study of the properties of thin, compact oxide films (Pd α -oxides) formed at polycrystalline Pd wire electrodes and at Pd-sputter-coated quartz crystals (to enable *in situ* mass measurements) in alkaline and neutral sulfate solutions has been carried out. In alkaline solutions, the mass of the film is consistent with the formation and reduction of $\text{Pd}(\text{OH})_2 \cdot \text{H}_2\text{O}$, in agreement with the *ca.* -58 mV pH dependence observed over a narrow alkaline pH range using solutions that do not lead to competitive anion adsorption effects. This film can be transformed, without a change of oxidation state or significant thickening, by a particular continuous potential cycling regime, to one which reduces at *ca.* 270 mV more negatively, consistent with the development of a deprotonated, charge compensated, hydrated oxide film, *i.e.*, $\text{Pd}(\text{OH})_2 \cdot y\text{H}_2\text{O} \cdot x\text{OH}^- \cdot x\text{Na}^+$. In neutral sulfate solutions, evidence for sulfate adsorption on the reduced Pd surface and in the early stages of α -oxide formation is seen. Nevertheless, the mass of the α -oxide film could be measured, indicating it to be $\text{PdO} \cdot \text{H}_2\text{O}$ in this medium.

The electrochemical formation of a thin, compact α -oxide film on polycrystalline Pd surfaces is known to occur in a wide range of acidic and alkaline solutions. Despite the fact that PdO is widely considered to be the most stable form of the thermally formed Pd oxides, a substantial amount of controversy exists in the literature as to the oxidation state, composition and structure of the electrochemically formed α -oxide film. From electrochemical and XPS studies, some researchers have suggested that only PdO can be formed at potentials negative of the oxygen evolution reaction (OER),¹⁻⁴ whereas others support the formation of PdO_2 in this potential range.⁵⁻¹¹ PdO_3 has also been suggested to be the identity of the Pd α -oxide film, both at potentials near the onset of the OER⁷⁻¹¹ and at potentials more positive than this.

There are several reasons for the uncertainties in the nature of the Pd α -oxide film. Although PdO is known to be very stable,¹² Pd oxides of higher oxidation states, such as PdO_2 and PdO_3 , can undergo decomposition to PdO under open-circuit conditions in aqueous solutions and under high vacuum conditions.⁵ Because of this, the XPS response would identify the oxide as PdO even when the electrochemical data might predict an oxide film of higher oxidation state or of different composition. In addition, the absolute stoichiometry of the Pd oxides cannot be deduced readily from XPS studies because of the overlay of the Pd $3p_{3/2}$ and the O 1s peaks in the XPS spectrum.^{4,5} Further lack of certainty regarding the nature of electrochemically formed Pd oxide films results from the unknown amount of water in the films. It also remains unclear as to whether these oxides might be in the hydroxide form, *i.e.*, $\text{Pd}(\text{OH})_2$ or $\text{Pd}(\text{OH})_4$.^{4,5}

In our previous published work concerning the electrochemical behaviour of Pd,¹³ a detailed examination of the impedance response of thin α -oxide films was carried out. This work revealed principally that these Pd α -oxide films are non-conducting, dielectric materials and that uniform film growth occurs at constant anodic potentials in both acidic and alkaline solutions. However, there are some distinctive differences between the Pd α -oxide films formed and studied in alkaline *vs.* acidic solutions. The most notable is the presence of a relatively large pseudocapacitance in alkaline, but not in acidic, solutions; this was interpreted¹³ as representing an adsorbed surface species, either adsorbed hydroxide ion or water, in alk-

aline solutions, both on the α -oxide surface and on the reduced Pd metal surface. In our other work regarding Pd,¹³⁻¹⁷ we have examined the growth mechanism and the properties of thicker, hydrous, Pd β -oxide films, formed at potentials substantially more positive than that of the OER. The β -oxide films were studied using a mixture of electrochemical techniques, as well as high-resolution TEM structural analysis methodologies.

In the present work, *in situ* mass measurements have been carried out in alkaline and neutral solutions during the growth and reduction of Pd α -oxide films, with the goal being to obtain further insight into the oxidation state, structure and composition of these films. Acidic solutions were not examined in detail in this mass measurement work owing to the known propensity for Pd dissolution in acidic media. It has been shown that during potential cycling in 1 mol dm⁻³ sulfuric acid, the rate of Pd dissolution is *ca.* 30-40 times that of Pt,¹⁸ with the highest dissolution rates existing in the early stages of α -oxide formation and also concurrently with Pd oxide reduction.^{7,19} The dissolution of Pd in acidic solutions concurrently with oxide growth and reduction would make the interpretation of the *in situ* mass gain/loss data very complex, and could also seriously limit the lifetime of the Pd-coated quartz crystals.

Experimental

Equipment

An EG&G 173 potentiostat and a 175 universal programmer were used for the cyclic voltammetry (CV). The resulting *E-I* curves were recorded using either an HP 7045B or a BBC SE 780 X-Y recorder. A Pierce-type oscillator²⁰ and a Philips PM6654C high-resolution frequency counter-timer were employed for the quartz crystal microbalance (QCMB) work.

Electrodes and cell

A polycrystalline Pd wire (1 mm diameter, 0.3-1.0 cm length, 99.9% purity, Aldrich), sealed in soft glass tubing, was used as the working electrode (WE) in the preliminary electrochemical

experiments. *In situ* mass measurements were carried out using AT-cut quartz crystals (2.5 cm in diameter, Valpey-Fisher), first sputter-coated with an undercoat of Cr to a thickness of *ca.* 50 nm followed by Pd to *ca.* 450 nm. Electrical contact was made to each side of the crystal with Au wires using conducting silver epoxy. The frequency-to-mass conversion factor²⁰ was $56.6 \text{ Hz } \mu\text{g}^{-1} \text{ cm}^2$. The electrochemically active surface area of both the Pd wire and the Pd-sputter-coated quartz crystals was determined from the charge passed during the reduction of α -oxide film formed in a slow sweep scan to 1.3 V *vs.* RHE. This has been reported²¹ to be equivalent to a charge density of 0.42 mC cm^{-2} , yielding roughness factors of 1.7 for the wire and 1.3 for the Pd-coated crystals.

A two-compartment glass cell was used in all of this work, with the quartz crystal sandwiched horizontally between two rubber O-rings at the base of the main compartment. The Pd surface area exposed to the cell solution was either 0.45 or 0.5 cm^2 , as indicated. The counter-electrode in all experiments consisted of a large area Pt gauze, placed in the same compartment as the WE, while the reference electrode (RE), placed in the second compartment, was a reversible hydrogen electrode (RHE) in the 1 mol dm^{-3} NaOH experiments and a standard saturated calomel electrode (SSCE) [0.236 V *vs.* standard hydrogen electrode, SHE] in the experiments carried out in Na_2SO_4 and NaClO_4 solutions.

Solutions and general experimental conditions

Electrochemical and QCM measurements were made either in 1 mol dm^{-3} NaOH or 1 mol dm^{-3} Na_2SO_4 solutions. These solutions were made up using ACS grade chemicals (Fisher) and deionized, doubly-distilled water. All solutions were thoroughly deaerated by bubbling nitrogen initially through, and later over, the cell solution. Alkaline solutions of constant ionic strength were made up for the pH dependence studies using NaClO_4 as the supporting electrolyte. All of the experiments were carried out at room temperature, *i.e.*, *ca.* 23 °C.

Results and Discussion

General electrochemical behaviour of Pd α -oxide films

Fig. 1(a) and (b) show the typical CV response of a polycrystalline Pd wire in 1 mol dm^{-3} H_2SO_4 and in 1 mol dm^{-3} NaOH solutions, respectively. In the acidic medium, it can be seen that the oxidation of Pd commences at *ca.* 0.75 V and continues in the anodic plateau (A_1), with oxygen evolution (OER) commencing noticeably at *ca.* 1.5 V. In the reverse scan from the upper limit of 1.6 V, only a single cathodic peak (C_1) is seen, suggesting that a single type of oxide film is formed and reduced at Pd electrodes under these conditions. Similar to Fig. 1(a), the CV of Pd in base [Fig. 1(b)] also demonstrates the formation of the α -oxide film in a plateau (A_1) and a corresponding reduction peak (C_1). However, Pd α -oxide film growth commences at *ca.* 0.6 V in alkaline solutions and overlaps much more than in acidic solutions with the hydrogen oxidation process [seen at 0.2–0.6 V in Fig. 1(b)]. The α -oxide formation occurring at more positive potentials in sulfuric acid solutions might be a result of blocking of the Pd surface by adsorbed HSO_4^- , similar to what has been reported for Pt and Au electrodes in sulfuric (*vs.* perchloric) acid solutions.^{6,22} It is also possible that the greater than –59 mV pH dependence of the Pd/Pd α -oxide reaction might reflect some deprotonation of the oxide in alkaline solutions. It has been reported previously that the onset potential for Pd α -oxide formation has a *ca.* –72 mV pH dependence over the entire pH range by Burke *et al.*,^{23,24} this was interpreted as reflecting an anionic charge borne by the α -oxide film at all pH values.

Further evidence for differences in the Pd α -oxide electrochemistry as a function of pH can be seen by the appearance

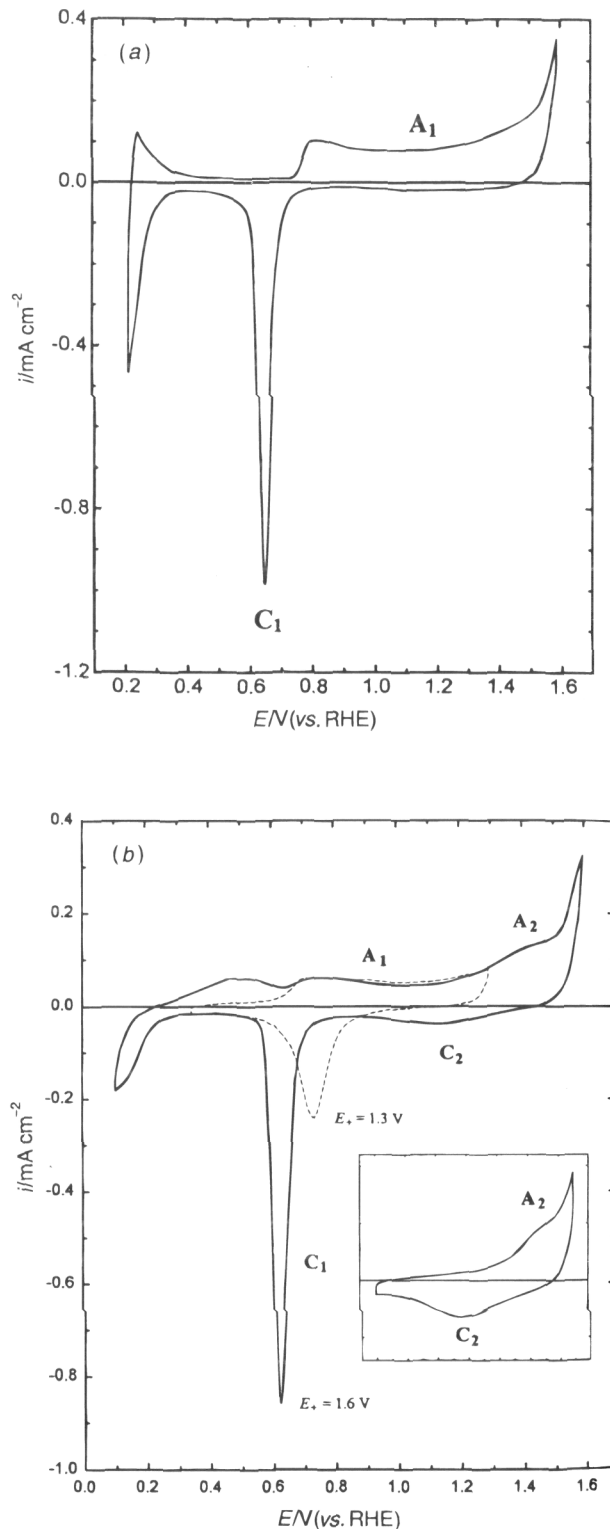


Fig. 1 Typical CV response for polycrystalline Pd wire in (a) 1 mol dm^{-3} H_2SO_4 ; $\nu = 50 \text{ mV s}^{-1}$ and (b) 1 mol dm^{-3} NaOH at $E_+ = 1.6 \text{ V}$ (—) and 1.3 V (---); $\nu = 50 \text{ mV s}^{-1}$

of a second pair of redox peaks (A_2 and C_2) centred at *ca.* 1.3 V in alkaline solutions. Although controversy exists in the literature in terms of the assignment of the A_1/C_1 and A_2/C_2 CV features, it seems reasonable to suggest that the A_1/C_1 process reflects the formation/reduction of a thin Pd^{II} oxide film at all pH values, whereas the A_2/C_2 peaks seen in basic media are most likely to represent a Pd^{II}/Pd^{IV} oxide transition. The A_2/C_2 peaks have been suggested^{3,4,7–9} as representing the PdO/PdO₂ redox equilibrium.

In the QCMB study of thin surface films formed electrochemically it is important to examine the mass change as a function of charge passed for films of varying thickness, in order to establish the true mass of the film, rather than measuring only net mass changes owing to exchange processes at the electrode surface for monolayers. In this work, it was recognized that the formation of thicker α -oxide films by sweeping to increasingly positive potentials would have associated with it the risk of forming a second, quite different type of oxide film, *i.e.*, the hydrous β -oxide film, believed to be a hydrated Pd^{IV} or even a Pd^{VI} oxide film of very different properties.^{1,14,24} In addition, α -oxide films formed in a potential sweep to different anodic potential limits might differ in their composition, structure, *etc.*, from those formed under more controlled conditions, *i.e.*, at constant potential. Furthermore, higher potentials increase the likelihood of Pd dissolution, even in neutral and alkaline solutions, which would be problematical in these QCMB experiments. For these reasons, α -oxide films were formed to various thicknesses by remaining at a constant potential for various lengths of time, followed by film reduction in a cathodic sweep during which the mass loss was measured. As seen in Fig. 1(b), there is a danger of formation of Pd hydride at potentials lower than *ca.* 0.2 V in alkaline solutions. For this reason, the potential of the Pd-coated quartz crystals was always maintained positive of 0.3 V in all of this work.

Fig. 2(a) shows a typical set of CVs obtained during the formation, with time of holding at 1.3 V, and subsequent reduction, at 50 mV s⁻¹, of Pd α -oxide films in 1 mol dm⁻³ NaOH. It can be seen that the CV response of the sputtered-Pd electrode, which was found to be linearly dependent on the

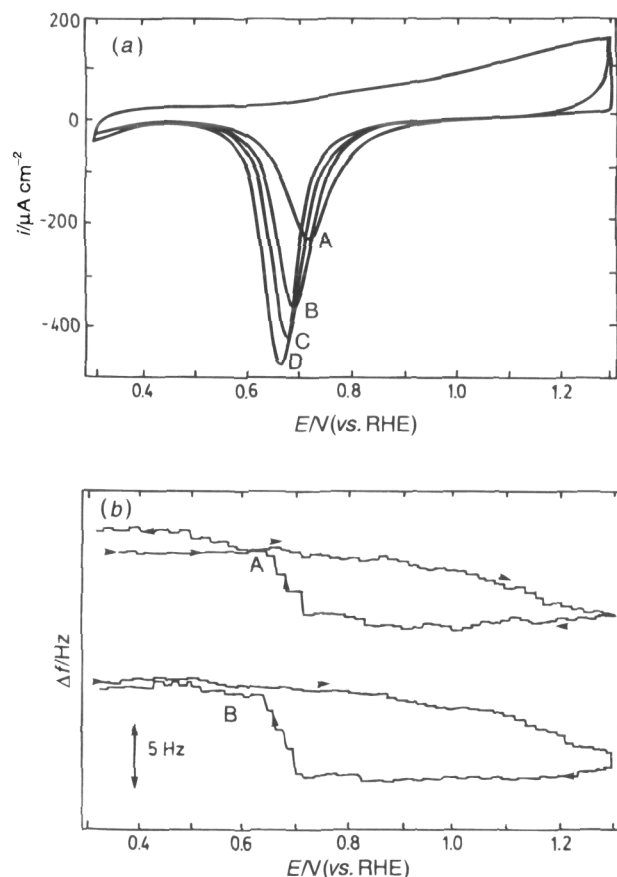


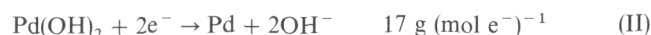
Fig. 2 (a) CV response during Pd α -oxide film reduction at Pd-coated quartz crystal after 0 (A), 0.5 (B), 2 (C) and 10 (D) min growth in 1 mol dm⁻³ NaOH at 1.3 V; ν = 50 mV s⁻¹; electrode area = 0.45 cm². (b) Frequency vs. potential plots corresponding to (a) after 0 (A) and 0.5 (B) min at 1.3 V; ν = 50 mV s⁻¹.

sweep rate, is very similar to that of the Pd wire electrode [Fig. 1(b)]. Oxide film reduction peaks move negatively with time of holding, *i.e.*, with the amount of α -oxide film formed, similar to the well-known behaviour of Pt α -oxide film formation/reduction.^{25,26} Fig. 2(b) shows several of the frequency (mass) change vs. potential plots recorded during oxide film reduction. The mass change data tracks the CV well, with a mass increase seen to commence at the same potential in the positive sweep as the anodic currents begin to rise, *i.e.*, at *ca.* 0.65 V, and the principal mass loss is seen precisely over the potential range of the cathodic peak. Notably, the mass of the electrode appears to be relatively independent of potential between *ca.* 0.3 and 0.6 V, suggesting that no measurable changes occur in terms of the state of the electrode surface under these conditions, *i.e.*, the amount of adsorbed water and/or electrolyte does not seem to change as a function of potential. In some experiments, the frequency at low potentials differed before and after oxide growth at constant potential and subsequent oxide reduction in alkaline solutions, as seen in Fig. 2(a), curve A. This may reflect the loss, by dissolution, of some Pd and/or underlying Cr, with time spent at positive potentials. This is one reason why the α -oxide mass data was taken primarily from the reduction sweep, which would be expected to be free of the problems of metal dissolution.

Table 1 provides the mass changes and integrated cathodic charge densities obtained for the single sweep (no hold) condition as well as for holding times at 1.3 V for 0.5, 1, 2, 4, 7 and 10 min for a typical experiment. Table 1 also summarizes these data in terms of the mass change per mole of electrons passed during Pd α -oxide reduction. This ratio is seen to be essentially independent of the amount of oxide film formed or of such variables as the potential sweep rate used during oxide reduction, hence probably correctly reflecting the properties of the α -oxide film formed at these sputter-deposited-Pd electrodes at 1.3 V in alkaline solutions. Very similar results were obtained with six different Pd crystals in six different sets of experiments; in each case, the average mass of the film per mole of electrons [g (mol e⁻)⁻¹] passed either during its formation or reduction was *ca.* 25–27 in 1 mol dm⁻³ NaOH solutions.

In order to test the validity of these results further, another series of experiments was carried out in which the mass change was monitored during oxide film growth and reduction in single sweep experiments to upper potential limits ranging from 1.3 to 1.6 V, being careful to remain negative of the potentials at which the hydrous β -oxide film can form. These results are also shown in Table 1, indicating that again, an average mass loss of *ca.* 26 g (mol e⁻)⁻¹ was monitored in each case.

This film mass of *ca.* 26 g (mol e⁻)⁻¹ appears to be quite high, especially when compared with the theoretical mass changes (considering the mass per mole of film material lost from the surface per mole of electrons passed) for reactions that are likely to be occurring in the A₁/C₁ CV features. Reactions (I) and (II) consider the α -oxide film to be PdO and the hydroxide form, Pd(OH)₂, respectively, without any consideration of adsorbed surface species.



Comparatively low mass ratios of 8 and 17 g (mol e⁻)⁻¹ passed are predicted, respectively.

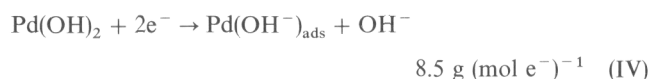
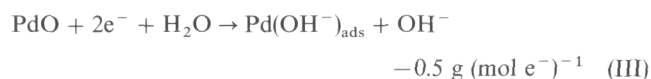
If it were assumed that the α -oxide film involves Pd in the +IV oxidation state in the above reactions, *i.e.*, PdO₂ and Pd(OH)₄, the mass change per electron ratio will not be affected. This indicates an interesting limitation of these experiments, namely that these QCMB results cannot yield the oxidation state of the metal in the oxide film, but rather

Table 1 Mass and charge density data for Pd α -oxide film reduction in 1 mol dm⁻³ NaOH solutions

α -oxide films formed with time spent at 1.3 V (surface area = 0.45 cm ²)			
t/min	$\Delta f/\text{Hz}$	$q/\text{mC cm}^{-2}$	mass/g (mol e ⁻) ⁻¹
0	5.4	0.19	23.4
0.5	8.0	0.25	26.4
1.0	7.2	0.27	22.0
2.0	8.4	0.28	24.7
4.0	9.3	0.30	25.5
7.0	12.0	0.35	28.2
10.0	13.4	0.38	29.0
			av. 25.6 (± 2.5)
α -oxide films formed in single sweep to various upper potential limits (surface area = 0.5 cm ²)			
$E_+/\text{V vs. RHE}$	$\Delta f/\text{Hz}$	$q/\text{mC cm}^{-2}$	mass/g (mol e ⁻) ⁻¹
1.3	5.4	0.17	29.1
1.4	6.4	0.23	24.6
1.5	8.0	0.29	25.3
1.6	10.4	0.34	28.0
			av. 26.7 (± 2.1)

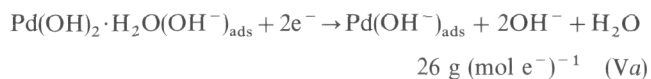
can only provide compositional information. Because the literature is in general agreement that Pd in electrochemically formed α -oxide films is in the +II oxidation state,¹⁻⁴ all proposed formulations for the Pd α -oxide film will be consistent with this in the present work.

It is also noteworthy that if adsorbed water and/or hydroxide ion is assumed to be present on the reduced metal surface only and not on the oxide surface as well, the predicted mass to charge ratios will be still lower, *e.g.*,



Therefore, the relatively high ratios shown in Table 1 must reflect a more complex, heavier oxide film than those suggested in reactions (I)–(IV).

One possible form of the Pd α -oxide that would be consistent with the relatively high mass observed is given in reaction (V). It consists of the oxide film as a hydrated Pd^{II} hydroxide material, not inconsistent with the alkaline medium under consideration here. Reaction (Va) is basically the same as (V), although the presence of an adsorbed surface species, *i.e.*, OH⁻, on both the oxide surface and on the reduced metal surface, is shown in order to be consistent with the results of our earlier impedance studies in alkaline solutions.¹³



PdO · 2H₂O is another possible form of the α -oxide film that would also yield theoretical mass data, which would fit the experimentally observed results [reaction (VI)]. However, there is no literature support for this form of Pd oxide and therefore it is considered to be an unlikely film product under these conditions.



Reactions (V), (Va) and (VI) predict a -59 mV pH dependence for the Pd/ α -oxide equilibrium. In order to provide further support for this reaction in alkaline solutions, specifi-

cally for reaction (V), the effect of the OH⁻ concentration on the observed potential of this equilibrium was examined over a relatively narrow alkaline pH range, and employing a non-adsorbing electrolyte, *i.e.*, NaClO₄, in order to maintain a constant ionic strength. Oxide films were grown in a 1 mol dm⁻³ NaOH + 1.5 mol dm⁻³ NaClO₄ solution and then reduced in solutions of different pH but of the same ionic strength. Because the ionic strength of these solutions is very high, *i.e.*, *ca.* 2.5 mol dm⁻³, the Debye-Hückel law and even the Davies' modification of the law²⁷ are no longer valid and therefore the solution pH cannot be calculated. However, the activity coefficients will be close to constant in these experiments and, therefore, the relative concentration of OH⁻ can be controllably altered. Fig. 3 shows a plot of the C₁ peak potential, measured at a 20 mV s⁻¹ sweep rate, *vs.* the OH⁻ concentration. The slope of the plot, which would have been the same for the potential at the onset of α -oxide film formation, is -57.7 mV per pH unit. This is very close to the -59 mV slope expected for the hypothesized reaction (V).

Burke *et al.*^{23,24} suggested that the α -oxide film exhibits a -72 mV pH dependence, particularly at the onset of its formation, which would be consistent with the following formulation for the oxide reaction [reaction (VII)], which predicts a -75 mV pH dependence. The presence of an adsorbed species on both the oxide and the reduced Pd surface is also included here.

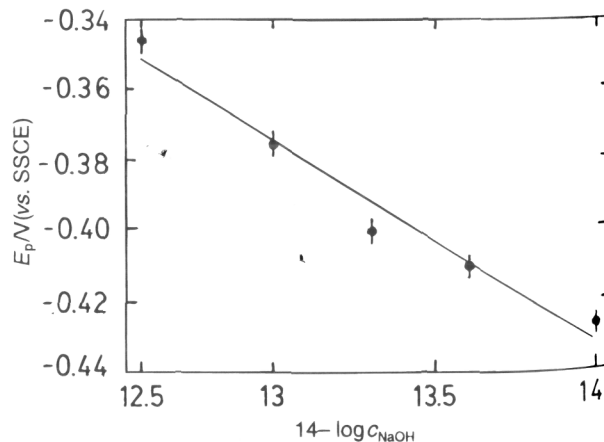


Fig. 3 pH dependence of the C₁ peak during reduction of α -oxide film formed in 1 mol dm⁻³ NaOH + 1.5 mol dm⁻³ NaClO₄ and reduced at 20 mV s⁻¹ in solutions of different OH⁻ concentration but of constant ionic strength



The co-adsorption of hydroxy groups and alkali-metal ions at high pH has also been suggested in a recent QCMB study of sputter-coated-Au crystals by Kautek *et al.*²⁸ However, based on the experimental pH dependence of peak C₁, Fig. 3 disagrees with this interpretation of the mass measurement data and, therefore, reaction (V) is still considered to be the most appropriate. The α -oxide film formed in 1 mol dm⁻³ NaOH solutions is therefore suggested to be Pd(OH)₂·H₂O.

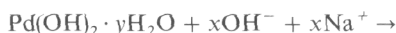
Transformation of Pd α -oxide by continuous potential cycling

It was reported by Jeong *et al.*¹¹ that long times of potential cycling at 50 mV s⁻¹ between 1.5 and 0.65 V resulted in the transformation of the α -oxide film to a different state, as seen by a significant negative shift of its reduction peak. It was suggested¹¹ that this reflected the conversion of the α -oxide film (in an unspecified state) to PdO₃, with no discussion provided regarding the mechanistic origin of PdO₃. However, our studies indicate that a different interpretation is warranted. Also, this transformation process seems to shed further light on the composition and nature of thin, electrochemically formed oxide films at Pd surfaces, in general.

Fig. 4 shows a typical set of CV reduction profiles for α -oxide films formed at a polycrystalline Pd wire electrode immediately after growth in a scan to 1.5 V in 1 mol dm⁻³ NaOH (···) and then after potential cycling for 10 (---) and 30 (—) min between 0.65 and 1.5 V. In this potential range, the α -oxide film cannot be readily reduced and each cycle involves a potential excursion over the A₂/C₂ peaks. It is clear that a significant change in the Pd oxide film results from this continuous cycling procedure. After cycling for 30 min, the C₁ peak has shifted negatively by ca. 280 mV and, significantly, the total cathodic charge in the peak, now labelled as C'₁, has increased only by ca. 25% as compared with the original C₁ peak charge density. An increase by a factor of 1.5–3 should have been observed if this transformation process involved the

conversion of either a Pd^{IV} oxide or a Pd^{II} oxide to PdO₃, respectively. Moreover, when a similar experiment to that in Fig. 4 was carried out, but in which the upper potential limit was maintained negative of peak A₂ throughout the cycling process, *e.g.*, 1.3 V, only the normal C₁ peak was seen, although ca. 20% larger and shifted a little negatively owing to the normal film thickening, which is known to occur with time at positive potentials.

These results indicate that the conversion of the α -oxide film does not involve a change in the oxidation state of Pd but, more likely, a change in the film composition. It is suggested that continuous cycling over the A₂/C₂ peaks, which has been considered^{13,15} to involve the conversion of at least the surface of the α -oxide film to a Pd^{IV} oxide [*e.g.*, to Pd(OH)₄·H₂O in alkaline solutions] and back, might promote further hydration of the α -oxide film, forming Pd(OH)₂·yH₂O (y > 1). This film might then be converted to an anionic form by the addition of OH⁻; Na⁺ would then serve as the charge compensating cation [reaction (VIII)].



(formed with cycling between 0.65 and 1.5 V) (VIII)

The reduction process that occurs in peak C'₁ would then be depicted by reaction (IX) (adsorbed surface species are not shown here).



(peak C'₁) (IX)

Reaction (IX) would be expected to occur at a more negative potential than reaction (V), consistent with the more negative potential of peak C'₁ vs. C₁ in Fig. 4.

In situ mass measurements of Pd α -oxide films in neutral solutions

Preliminary QCMB studies in acidic media, normally sulfuric acid, showed that the Pd-coated crystals were readily dissolved in acidic media. Therefore, the study of the effect of pH on the oxide film response was examined only in neutral Na₂SO₄ solutions in this work. Fig. 5(a) shows the α -oxide reduction CV profiles after various times of holding at 0.8 V vs. SSCE (ca. 1.3 V vs. RHE) in this medium. The α -oxide reduction peaks can be seen to be broader and centred at more negative potentials than for base [Fig. 1(b) and 2(a)]. One concern might have been the development of a local pH during oxide film reduction in these unbuffered neutral solutions. However, the shift in the oxide reduction peak potential with the amount of α -oxide film formed in these neutral solutions, as well as with potential sweep rate, is very similar to that observed in alkaline solutions and argues against any local pH effects in these experiments. Fig. 5(b) shows the frequency response after 'no hold', and a 30 s and 4 min hold at 0.8 V, over the full potential range in both the anodic and cathodic scans.

It is of interest that, in the anodic scan in the potential range from ca. -0.5 to -0.1 V vs. SSCE, a frequency increase, *i.e.*, a mass loss, is observed, which is contrary to the essentially constant mass observed under these conditions in alkaline solutions [Fig. 2(b)]. As no evidence was obtained for a change in the extent of water adsorption on Pd electrodes with increasing potential in the double layer range using this technique in alkaline solutions, the results of Fig. 5(b) suggest that sulfate ion is playing a role in these experiments, similar

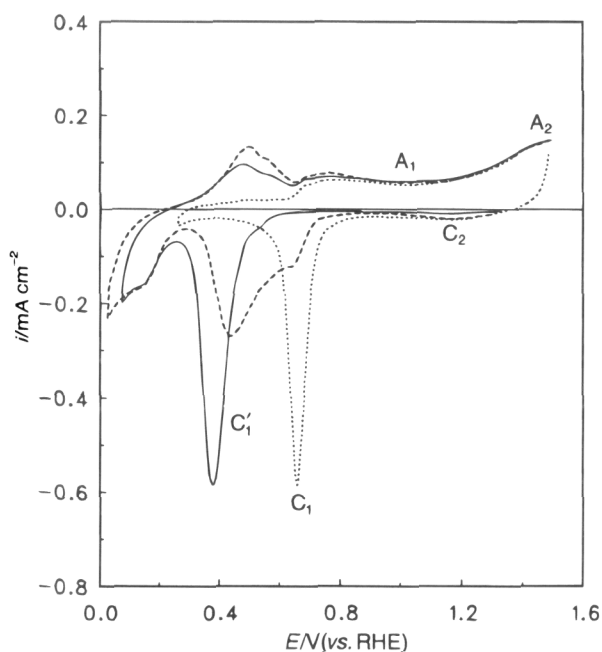


Fig. 4 CVs of polycrystalline Pd wire electrode in 1 mol cm⁻³ NaOH after 10 (---) and 30 (—) min of potential cycling between 0.65 and 1.5 V at 50 mV s⁻¹, as compared with the reduction profile of a freshly formed Pd α -oxide film (···)

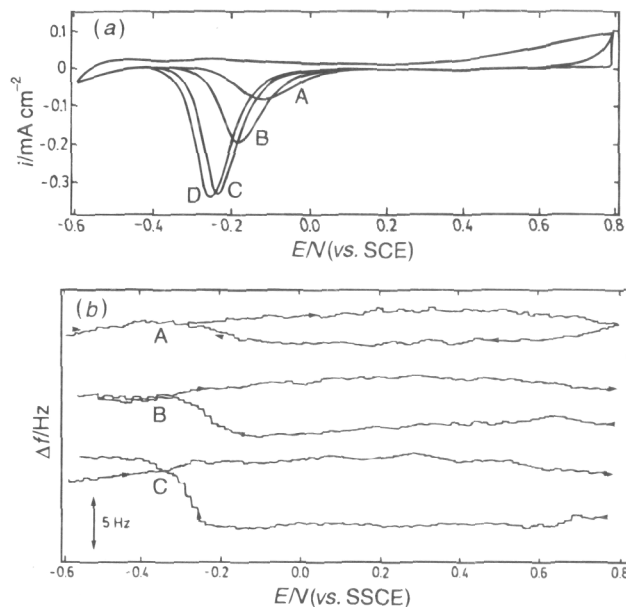


Fig. 5 (a) CV response during Pd α -oxide film reduction at Pd-coated quartz crystal after 0 (A), 0.5 (B), 4 (C) and 7 (D) min at 0.8 V vs. SSCE in 1 mol dm⁻³ Na₂SO₄; $\nu = 50$ mV s⁻¹; electrode area = 0.5 cm². (b) Frequency vs. potential plots corresponding to Fig. 5(a) after 0 (A), 0.5 (B) and 4 (C) min at 0.8 V vs. SSCE in 1 mol dm⁻³ Na₂SO₄; $\nu = 50$ mV s⁻¹.

to that reported for Pt in sulfate-based solutions,²² for Pd in sulfuric acid⁶ and in NaOH solutions containing added sulfate ion.²⁹ The present results indicate that as α -oxide film formation commences sulfate ions are being desorbed from the surface, as seen by the net mass loss under these conditions. Owing to these competitive adsorption effects during the early stages of α -oxide growth it was considered essential to examine the oxide film mass as a function of film thickness, in an attempt to measure the bulk film properties rather than only the exchange processes at the electrode surface for sub-monolayer oxide formation/reduction.

Table 2 shows the results obtained for up to 10 min of α -oxide film growth in the neutral sulfate solution. It can be seen that with an increasing amount of film, the mass per mole of electrons increases, from ca. 13 for the first monolayer of film to an apparent steady-state value of ca. 17 g (mol e⁻)⁻¹. It is also of interest that, after the reduction of these somewhat thicker α -oxide films, the frequency remains constant in the negative scan to ca. -0.6 V, indicating that the surface is, at least at this stage, apparently free of anion adsorption effects. It is only after some time at cathodic potentials, followed by a subsequent anodic scan, that the frequency is seen to decrease and then increase again in the positive scan, indicative of the re-adsorption of sulfate with time at negative potentials and then the replacement of adsorbed sulfate by the α -oxide film at more positive potentials.

Table 2 Mass and charge density data for Pd α -oxide film reduction in 1 mol dm⁻³ Na₂SO₄ solutions (surface area = 0.5 cm²)

<i>t</i> /min	Δf /Hz	<i>q</i> /mC cm ⁻²	mass/g (mol e ⁻) ⁻¹
0	2.2	0.15	12.9
0.5	3.8	0.26	12.9
1	4.6	0.30	13.5
2	6.3	0.35	15.9
4	6.8	0.38	15.8
7	7.8	0.40	17.2
10	8.4	0.42	17.6

Assuming that the true mass to charge ratio is ca. 17 g (mol e⁻)⁻¹, the following reactions might reflect the α -oxide reduction process in neutral sulfate solutions (the presence of any additional adsorbed surface species is ignored here).



Both reactions (II) and (X) would predict a ca. -59 mV pH dependence, shown to be the case at least in alkaline solutions (Fig. 3) and probably the case throughout the pH range (the apparent pH dependence reported by others^{23,24} might be largely a result of anion adsorption effects, especially in acidic media and in the presence of sulfate ion, as was found in the present work).

PdO · H₂O has been reported to have a particular stability³⁰ in acidic and neutral solutions. Also, in the many prior studies of polycrystalline Pd electrodes carried out in acidic media, the α -oxide film has been suggested to be in the PdO form.^{1-4,10,12,30} Therefore, it seems reasonable that in these sulfate-based near-neutral solutions (pH ca. 5), the oxide might be more similar to that formed in acidic sulfate solutions and less like that formed in basic media. Therefore, the proposed hydration of PdO, forming PdO · H₂O, seems reasonable and certainly matches the mass measurement data. It is also of interest that in our previous QCMB study of Pt α -oxide films formed at Pt electrodes in sulfuric acid solutions,³¹ the results indicated a mass change of ca. 8 g (mol e⁻)⁻¹ passed and the oxide film was therefore suggested to be PtO (or PtO₂), i.e., a non-hydrated oxide, consistent with the above argument. Pt-coated quartz crystals could be studied readily in acidic solutions owing to the much lower rate of dissolution of Pt in this medium than is the case for Pd.^{7,19}

If an excess negative charge had been suggested for the α -oxide formed in the neutral Na₂SO₄ medium by the presence of additional OH⁻ in the film, the charge compensating cation would probably be Na⁺, which would result in too large a film mass, as compared with that observed. Also, if sulfate ion is assumed to be part of the film structure, again, the film mass would have been still higher due to the large mass of the sulfate ion. Therefore, based on the mass data of Table 2, both of these alternative options for the composition of the Pd α -oxide film in neutral sulfate solutions are not considered likely.

Conclusions

1. The formation and reduction of thin Pd α -oxide films at Pd-sputter-coated quartz crystals in alkaline solutions involves a mass change of ca. 26 g (mol e⁻)⁻¹ passed. Based also on the observed -57.7 mV pH dependence of this reaction in alkaline solutions, which were made up using non-adsorbing electrolyte, the film product is proposed to be Pd(OH)₂ · H₂O.

2. The α -oxide film can be transformed to a different state by employing a particular potential cycling regime in alkaline solutions. The film oxidation state does not change, as seen by the similar charge density to that of the normal α -oxide film, but the film can be reduced only at potentials ca. 270 mV more negative than usual. It is proposed that the film becomes more hydrated and also complexes with additional OH⁻, with Na⁺ as the charge compensating counter-ion, as a result of this treatment, forming Pd(OH)₂ · *y*H₂O · *x*OH⁻ · *x*Na⁺. This would be consistent with the more negative reduction potential observed.

3. In neutral sulfate solutions, a lower film mass of ca. 17 g (mol e⁻)⁻¹ is measured. Based on pH dependence arguments and the stability of various kinds of Pd oxides, it is proposed that the α -oxide film formed electrochemically in this medium is PdO · H₂O.

4. QCMB studies were not carried out in acidic solutions owing to the propensity for Pd dissolution at low pH.

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