

Voltammetric and galvanostatic studies of hydrous and anhydrous iridium oxide films.

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Electrolytically grown hydrous oxide films on iridium wire electrodes have been thermally treated from 473 to 773 K. Anhydrous oxide films formed by this treatment have been subjected to cathodic polarization at the potential of the hydrogen evolution reaction, square-wave pulsing of potential from -0.25 to $+1.25$ V with respect to SCE and to anodic galvanostatic polarization in 0.5 mol dm^{-3} H_2SO_4 . Cathodic pretreatment caused an increase of the voltammetric charge in the oxide formation region while the square-wave pulsing formed a hydrous oxide film whose voltammetric charge was superimposed on the charge of the anhydrous oxide film. Both procedures restored the hydrophilic nature of the electrode/solution interface. Potential-time curves during anodic galvanostatic polarization served as a diagnostic criterion for the stability and the state of the oxide film.

1. Introduction

The electrochemical properties of hydrous oxide films are of particular interest due to their application in electrocatalysis. The preparation, structure, acid-base properties and transport processes in the hydrous oxide films on noble metals have been reviewed recently by Burke and Lyons [1]. Experimental evidence of enhanced electrocatalytic activity of hydrous oxide films grown on iridium, ruthenium and rhodium for the oxygen and chlorine evolution reactions have been presented in a number of papers [2-6]. Their common properties in these reactions, particularly in the case of the oxygen evolution reaction (OER), are good electrocatalytic efficiency and low resistance to corrosion. Anhydrous oxide films, on the contrary, are less efficient but much more stable. There exists, therefore, for every metal oxide electrocatalyst, an optimum between stability and efficiency. This goal can be achieved by better understanding of electrochemical and surface properties of metal oxide electrodes.

While anhydrous oxide films on iridium are usually prepared by thermal decomposition of IrCl_3 on titanium as a substrate [7-9] hydrous oxide films are prepared electrolytically by triangular and/or square-wave potential pulsing in acid solution [10-21]. A convenient way to study both types of oxides is to prepare a hydrous oxide film electrolytically and treat it thermally. In recent papers from our laboratory we have studied electrochemical properties of electrodeposited and thermally treated oxide films of ruthenium on titanium [22, 23] and thermally treated hydrous oxide films on an iridium wire electrode [24]. In the case of iridium we have shown that the hydrous nature of the thermally treated film can be restored by potentiodynamic and square-wave pulsing i.e. by the

same procedures which form hydrous oxide film from a bare iridium electrode.

Some interesting effects of cathodic pretreatment of thermally prepared ruthenium oxide on titanium on its voltammetric properties at the potentials of the oxide formation have been reported recently by Ardizzone *et al.* [25]. These effects consisted in the change of the behaviour of the oxide layer after cathodic polarization. It is also the aim of the present work to examine voltammetric properties of the electrolytically grown hydrous oxide films on iridium followed by heat treatment after polarization at the potential range of the hydrogen evolution reaction.

The electrocatalytic properties of a metal oxide electrode, in the case of the OER for example, can be monitored by measuring the overpotential of the OER during anodic galvanostatic polarization. Any change in the state of the oxide film influences the overpotential of the OER. We have detected, using this procedure, a duplex oxide film on electrodeposited ruthenium in alkaline solution [22] and on iridium in acid solution [26]. The same procedure of anodic galvanostatic polarization was used in this work and the response of a thermally treated iridium oxide electrode, with and without cathodic pretreatment, on anodic polarization is presented.

2. Experimental details

2.1. Preparation of the oxide films

The iridium electrode was a wire of 0.5 mm diam., 0.25 cm^2 area, 99.9% purity (Goodfellow Metals) sealed into glass. The hydrous oxide film was grown by square-wave pulses from -0.25 V to $+1.25$ V with respect to the saturated calomel electrode (SCE) at

frequencies of 2 Hz for 5 min in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$. A cyclic voltammogram at a sweep rate of 50 mV s^{-1} was recorded from -0.25 V to $+1.2 \text{ V}$ in order to characterize the oxide film. The scan was terminated at -0.25 V and the electrode was transferred to the oven in its reduced state. Thermal treatment was carried out in air for 1 h.

2.2. Experimental set-up

Potentiodynamic, galvanostatic and coulometric measurements were carried out using an EG&G (Princeton Applied Research) 273/97 potentiostat/galvanostat. A three-compartment electrochemical cell, thermostated at $298 \pm 0.1 \text{ K}$ with a platinum foil as a counter electrode and SCE as a reference was used. Sulphuric acid (Fluka, Puriss.) was used without further purification.

2.3. The measurements

The charge integration of the cathodically polarized electrode was carried out in the following way. The electrode was held at -0.25 V for preselected periods of time. The potential was then stepped to $+0.1 \text{ V}$ (double layer region of the voltammetric curve) and held at this potential for 5 s. Within this period the cathodic charge was reset and a linear potentiodynamic scan at 50 mV s^{-1} sweep rate was performed up to $+1.2 \text{ V}$. The data in Tables 1 and 2, respectively, were determined by integrating the charge to preselected potentials, as indicated in Fig. 3a. The charge was read directly from the display of the 273/97 potentiostat/galvanostat.

Corrections for ohmic drop were made using a current interruption method with the Model 273/97 built-in current interruption technique. A typical value of the IR -drop at 30 mA was 30 mV , i.e. the solution resistance was 1Ω .

In order to use the same iridium wire electrode in subsequent measurements the thermally untreated hydrous oxide film was removed by boiling the electrode in hot aqua regia which dissolves a film within a few seconds. It is interesting to note that the thermally treated film was more stable. The removal of the oxide film from the surface of the thermally treated electrode was made more easy by square-wave activation from -0.25 to $+1.25 \text{ V}$. This procedure restored the hydrous nature of the oxide film which then dissolved in the aqua regia more rapidly.

Table 1. Voltammetric charge of thermally treated hydrous iridium oxide grown by square-wave activation (see Fig. 3a)

Temperature of thermal treatment	Charge (mC)			
	Q_{a1}	Q_{a2}	Q_{c1}	Q_{c2}
Untreated	10.95	5.49	4.42	9.23
473 K	4.58	2.04	3.88	1.76
573 K	3.40	1.74	2.82	1.12
673 K	3.54	1.94	2.54	0.98
773 K	3.12	1.56	1.86	0.74

Table 2. Voltammetric charge, of hydrous iridium oxide after thermal treatment and square-wave activation for 5 min

Temperature of thermal treatment	Charge (mC)			
	Q_{a1}	Q_{a2}	Q_{c1}	Q_{c2}
473 K	12.70	7.49	5.86	10.46
573 K	13.06	6.74	5.36	10.91
673 K	12.67	6.60	5.11	10.59
773 K	11.30	5.62	4.61	10.26

3. Results and discussion

3.1. Voltammetric charge after cathodic pretreatment of the thermally treated iridium electrode

Figure 1 shows the cyclic voltammogram when a hydrous iridium layer grown by square-wave pulses was thermally treated at 573 K . Before each scan the potential was held at -0.25 V for different periods of time. As can be seen there is little change in the anodic scan in the hydrogen region from -0.25 to 0.0 V , the charge decreases afterwards with increase of the holding time. There is an inflection point at $+0.5 \text{ V}$ where the charge starts to increase with holding time. During the whole anodic scan the balance of charge is positive. The increase of charge after $+0.5 \text{ V}$ is higher than its decrease up to $+0.5 \text{ V}$. In the cathodic scan the inflection point is at $+0.45 \text{ V}$, the balance of charge is, however, equal. The increase of charge in the more anodic region is accompanied by a decrease in the potential range from $+0.45$ to -0.15 V . The complete anodic/cathodic balance of charge is, therefore, positive which means that there is a certain amount of non-reduced oxide left on the electrode surface. Such a case of the partial reduction of the oxide has also been observed during potentiodynamic activation of the iridium electrode in acid solution [16, 21].

A common characteristic of the potentiodynamic profile of thermally treated electrolytically grown hydrous oxide films on iridium is a decrease of the voltammetric charge with the increase of the firing temperature [24] (see also Table 1). This observation

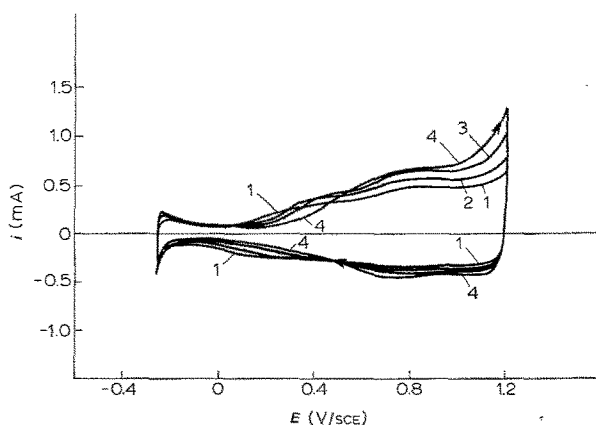


Fig. 1. Cyclic voltammograms at a sweep rate of 50 mV s^{-1} when the hydrous oxide film grown on iridium was thermally treated at 573 K and held at -0.25 V (SCE) in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ for 1 min (1); 5 min (2); 20 min (3); 60 min (4).

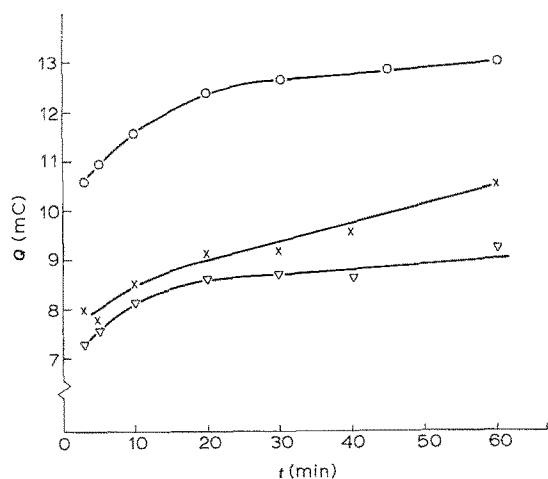


Fig. 2. Voltammetric charge from +0.1 to +1.2 V against holding time at -0.25 V for hydrous iridium electrode treated at 473 (O); 673 (x) and 773 K (∇), respectively.

also holds for an iridium electrode prepared by thermal decomposition [7]. It is also well known that a ruthenium oxide electrode behaves in many ways similarly to iridium. In a recent paper, Trasatti and co-workers [25] showed that the voltammetric charge of the ruthenium oxide electrode was increased by holding the electrode at the potential of the hydrogen evolution reaction. This phenomenon was explained by the wetting of hydrophobic sites of the oxide surface. The same phenomenon was observed in the present work, where various degrees of hydrophilicity of the oxide film were achieved by different temperatures of thermal treatment. Figure 2 shows the increase of the voltammetric charge with holding time at -0.25 V with respect to SCE for iridium electrodes treated at temperatures from 473 to 773 K. The increase of charge was obtained on all the investigated electrodes.

3.2. Voltammetric charge after square-wave pulsing of the thermally treated electrode

Cathodic pretreatment is not the only way of changing the electrochemical properties of an iridium oxide film. It was already shown [24] that holding a thermally treated hydrous oxide film on iridium at the potential of the oxygen evolution reaction, potentiodynamic and square wave activation of this electrode shifted the voltammetric charge to more anodic poten-

tials and restored the original potentiodynamic profile of the hydrous oxide film. The case of the square-wave activation of the thermally treated electrode was examined in more detail in this work.

Figure 3a shows a typical potentiodynamic profile of the hydrous iridium oxide film grown electrolytically in sulphuric acid. It is characterized by anodic peaks A_1 and A_2 with a shoulder preceding the A_1 peak. In the cathodic direction two peaks exist, C_2 and C_1 , respectively. The potential range where the voltammetric charges Q_{a1} , Q_{a2} , Q_{c1} and Q_{c2} have been integrated is also indicated. Figure 3b represents the potentiodynamic profiles when the hydrous oxide film shown in Fig. 3a was thermally treated at 473 K and when the thermally treated film was again subjected to square-wave pulses from -0.25 to $+1.25$ V at 2 Hz for 5 min. The double layer region is restored, i.e. the oxidation of the electrode starts at $+0.45$ V. However, the new anodic peak A'_1 at $+0.9$ V and the increase of all corresponding charges in comparison with those in Fig. 3a clearly indicate that the charge formed by a thermally treated film is superimposed on the charge of the newly formed hydrous oxide film. Table 1 shows the voltammetric charges when the hydrous oxide film was thermally treated at different temperatures. The anhydrous oxide films have been formed with the voltammetric charges which were significantly lower than the voltammetric charge of the thermally untreated oxide film. This is a common case when hydrous oxide films are thermally treated and the effect is due to a decrease in number of the hydrophilic sites responsible for proton and electron transfer in the redox processes in the oxide film. These anhydrous oxide films were again subjected to 5 min square-wave polarization and the corresponding charges are shown in Table 2. The charges are somewhat higher than those of activated but thermally untreated samples, (Table 1) which means that the hydrophilic nature of the oxide film has been restored in all the thermally treated samples. The only difference between the samples treated at 773 K and those treated at the lower temperatures is the absence of the double layer region of the voltammetric curve (Fig. 3b, Fig. 4). It means that in the case of the electrode treated at 773 K the voltammetric charge of the newly formed hydrous oxide film is superimposed on the charge of the anhydrous oxide film in the whole potential range.

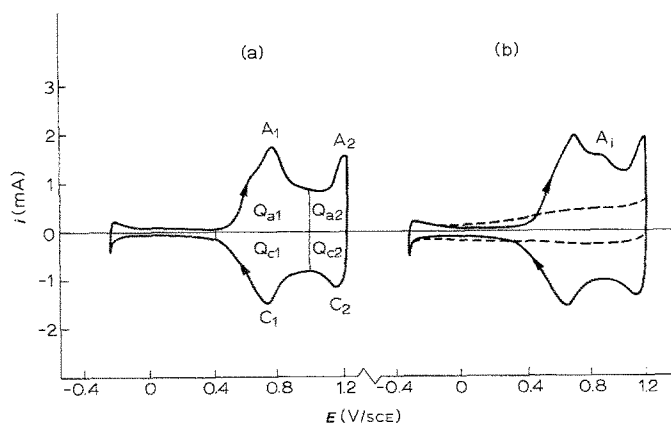


Fig. 3. Cyclic voltammogram at a sweep rate of 50 mV s^{-1} of hydrous iridium oxide grown by square-wave pulses from -0.25 V to $+1.25$ V at 2 Hz for 5 min in 0.5 mol dm^{-3} H_2SO_4 (a); cyclic voltammograms when this electrode was thermally treated at 473 K (dashed line) and, subsequently, by square-wave activation for 5 min (full line) (b).

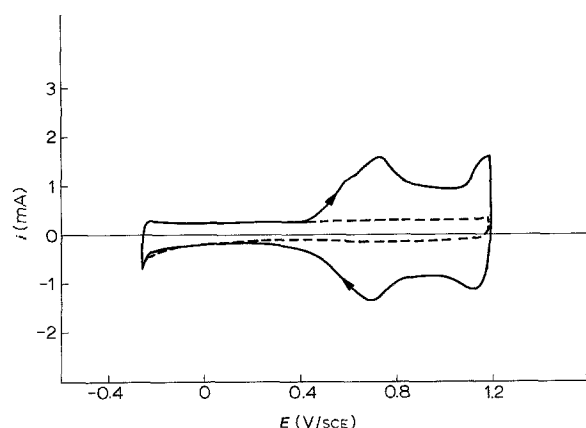


Fig. 4. Cyclic voltammograms at a sweep rate of 50 mV s^{-1} when the hydrous oxide film on iridium was thermally treated at 773 K (dashed line) and, subsequently, by square-wave activation for 5 min (full line).

The potentiodynamic profiles are also of the same form except for the disappearance of the A_1' peak.

3.3. Anodic galvanostatic polarization of thermally treated iridium electrode

The results presented so far show that the hydrophilic nature of a thermally treated film can be restored by either holding the electrode at -0.25 V or by square-wave activation. These changes can be monitored by measuring the overpotential of the OER during anodic galvanostatic polarization. The stability of the hydrous oxide film on iridium was examined in this way [26] where the sharp increase of overpotential of the OER was the indication for the dissolution of the hydrous oxide layer. The same experiment was carried out in this work with the hydrous iridium oxide electrode treated at 573 K. Figure 5 shows the change of overpotential of the OER as a function of time during anodic galvanostatic polarization at 30 mA. The overpotential of the thermally treated electrode which was held at -0.25 V for one hour starts at $+1.37 \text{ V}$ after switching anodic current. There is a continuous increase of overpotential which ends at $+1.57 \text{ V}$ when the hydrous layer was dissolved. This was also indicated by the cyclic voltammogram which showed the poten-

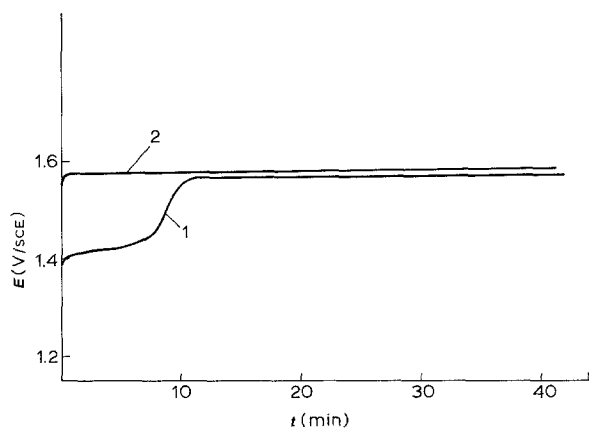


Fig. 5. Potential-time curves, corrected for IR -drop, during anodic galvanostatic polarization at 30 mA of thermally treated (573 K) hydrous iridium electrode held for one hour at -0.25 V (SCE) in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ (1); the same electrode without cathodic pretreatment (2).

tiodynamic profile of the bare iridium electrode. When the hydrous oxide film is dissolved the OER proceeds further on the compact inner oxide which is a few layers thick [21]. Curve 2 in Fig. 5 shows the overpotential of the thermally treated electrode. This electrode was taken from the oven, cooled to the room temperature, transferred to the electrochemical cell and galvanostatically polarized. Any electrochemical treatment which might restore some hydrophilic sites before galvanostatic polarization was, therefore, avoided. After switching anodic current the overpotential skipped to $+1.58 \text{ V}$ and remained unchanged. It is evident that the cathodically pretreated electrode has, at the beginning of the experiment, considerably lower overpotential which means better electrocatalytic properties. This electrode is less stable, however, in comparison with the electrode which was not cathodically treated.

4. Conclusions

Thermal treatment of electrolytically grown hydrous oxide films on iridium in sulphuric acid leads to various degrees of hydrophilicity of the surface which can be enhanced by either cathodic polarization or square-wave pulsing.

The voltammetric charge of the anhydrous oxide film decreased with the increase of the temperature of the thermal treatment. After square-wave activation of the anhydrous oxide film the hydrophilic sites were restored. The total voltammetric charge was even higher than the charge of the activated, but thermally untreated, oxide film and consisted of the charge of the newly formed hydrous oxide layer and of the charge of the anhydrous oxide.

Anodic galvanostatic polarization proved to be useful as a diagnostic criterion for the presence of anhydrous and hydrous oxide films during the oxygen evolution reaction in acid solution.

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References

- [1] L. D. Burke and M. E. G. Lyons, in 'Modern Aspects of Electrochemistry' (edited by R. E. White, J. O'M. Bockris and B. E. Conway), Plenum Press (1986) p. 109.
- [2] S. Gottesfeld and S. Srinivasan, *J. Electroanal. Chem.* **86** (1978) 89.
- [3] L. D. Burke and E. J. M. O'Sullivan, *ibid.* **97** (1979) 123.
- [4] E. J. Frazer and R. Woods, *ibid.* **102** (1979) 127.
- [5] J. Mozota, M. Vuković and B. E. Conway, *ibid.* **114** (1980) 153.
- [6] M. Vuković, H. Angerstein-Kozłowska and B. E. Conway, *J. Appl. Electrochem.* **12** (1982) 193.
- [7] S. Ardizzone, A. Carugati and S. Trasatti, *J. Electroanal. Chem.* **126** (1981) 287.
- [8] A. T. Kuhn and C. J. Mortimer, *J. Electrochem. Soc.* **120** (1973) 231.

- [9] K. C. Fukuda, F. Iwakura and H. Tamura, *Electrochim. Acta* **24** (1979) 363.
- [10] A. Capon and R. Parsons *J. Electroanal. Chem.* **39** (1972) 275.
- [11] D. A. J. Rand and R. Woods, *ibid.* **55** (1974) 375.
- [12] D. N. Buckley and L. D. Burke, *J. Chem. Soc. Faraday Trans. I* **71** (1975) 1447.
- [13] J. O. Zerbino, N. R. de Tacconi and A. J. Arvia, *J. Electrochem. Soc.* **125** (1978) 1266.
- [14] S. Gottesfeld and J. D. E. McIntyre, *J. Electrochem. Soc.* **126** (1979) 742.
- [15] S. H. Glarum and J. H. Marshall, *ibid.* **127** (1980) 1467.
- [16] J. Mozota and B. E. Conway, *Electrochim. Acta* **28** (1983) 1.
- [17] J. Augustynski, M. Koudelka, J. Sanchez and B. E. Conway, *J. Electroanal. Chem.* **160** (1984) 233.
- [18] H. Y. Hall and P. M. Sherwood, *J. Chem. Soc. Faraday Trans. I* **80** (1984) 135.
- [19] M. Peuckert, *Surface Sci.* **144** (1984) 451.
- [20] R. Kötzt, H. Neff and S. Stucki, *J. Electrochem. Soc.* **13** (1984) 72.
- [21] P. G. Pickup and V. I. Birss, *J. Electroanal. Chem.* **220** (1987) 83.
- [22] D. Čukman and M. Vuković, *Croat. Chem. Acta.* **62** (1989) 551.
- [23] M. Vuković, *Electrochim. Acta* **34** (1989) 287.
- [24] *Idem*, *J. Appl. Electrochem.* **17** (1987) 737.
- [25] S. Ardizzone, S. Fregonara and S. Trasatti, *J. Electroanal. Chem.* **266** (1989) 191.
- [26] D. Čukman and M. Vuković, *ibid.* **279** (1990) 283.