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Oxygen evolution reaction on thermally treated iridium oxide films

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The properties of electrochemically grown and thermally treated oxide films on iridium were examined by cyclic voltammetry and potentiostatic polarization at potentials of the oxygen evolution reaction in 0.5 mol dm^{-3} sulphuric acid. The oxide was grown by square wave pulses from -0.25 to $+1.25$ V vs SCE, a procedure much faster in comparison with potentiodynamic activation at the same frequency. The activated electrode, exhibiting low corrosion resistance during oxygen evolution, was subsequently stabilized by heat treatment. Optimal conditions between stability and electrocatalytic activity have been determined to be between 200 and 300° C.

1. Introduction

The interest in the electrochemistry of iridium arises from two possible applications. The first is in electrochemical energy conversion where the iridium electrode, next to RuO_2, exhibits the lowest oxygen overvoltage in acidic solutions [1]. Because the slowest step in water electrolysis is electron transfer at the oxygen electrode, much attention has been focused on the electrocatalysis of the oxygen evolution reaction (OER) on noble metals, as well as on the transition metal oxides [2–5]. The second possible application of iridium is in electro-optic display devices due to its electrochromic properties, where the change of colour between oxidative and reductive states of the metal takes place [6–8].

Considerable research efforts have centred on the electrochemistry of iridium and iridium oxide films [9–30]. Iridium oxide electrodes can be prepared by either a thermal decomposition method [14, 15] or electrochemically by continuous potentiodynamic cycling [11, 16]. The latter method forms a hydrous oxide film, which has better electrocatalytic properties for the OER in terms of a lower Tafel slope and higher current density in comparison with a bare metal electrode [31]. The OER on iridium and iridium oxide has been studied by electrochemical methods [32–37], and the electrochemical oxide path of Bockris [38] has been proposed by Damjanović *et al.* [37]. More recently the OER was also studied by X-ray photoelectron spectroscopy [39, 40].

All the previous research has confirmed the good electrocatalytic properties of iridium oxide films on one hand and the low resistance to corrosion on the other. For technological applications, however, the long-term stability of the electrode is a major requirement for a good electrocatalyst. In this connection it is the purpose of the present paper to examine the electrochemical properties of thick oxide films on iridium for the oxygen evolution reaction under conditions of prolonged polarization.

2. Experimental details

Iridium electrodes prepared from wire, 0.5 mm in diameter, 99.9% purity and exposed area of 0.25 cm^2 (Goodfellow Metals, UK), were sealed directly into glass. The oxide film growth was achieved by polarizing the electrode with square wave pulses from -0.25 to $+1.25$ V vs SCE at frequencies of 2 Hz in 0.5 mol dm^{-3} sulphuric acid. A potentiostat (Princeton Applied Research 173) and a function generator (Wavetek Mod. 164, USA) were used. Cyclic voltammograms

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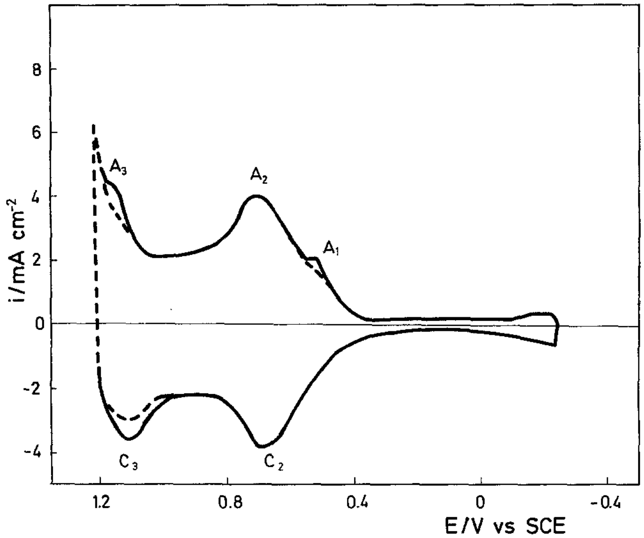

Fig. 1. Cyclic voltammogram at a sweep rate of $60 \mathrm{mV s^{-1}}$ of 55 min potentiodynamically activated (dashed line) and 2 min SQW-activated iridium electrode (full line) in $0.5 \mathrm{mol dm^{-3}}$ H_2SO_4 at a frequency of 2 Hz from -0.25 to $+1.25$ V vs SCE.

were recorded using an x–y recorder (Hewlett-Packard 7004B).

An H-shaped, three-compartment electrochemical cell with a platinum foil as a counter electrode and a SCE reference were used. Solutions were prepared using sulphuric acid (Fluka, Switzerland) and quadruply distilled water, the last two stages from a quartz still. Purified nitrogen and oxygen were bubbled, when necessary, through the solution.

3. Results

In this work, two procedures, triangular and square wave (SQW), frequently used in the electrochemical growth of oxide films on iridium [8, 11, 16], were examined. Fig. 1 shows cyclic voltammograms where both procedures resulted in almost identical potentiodynamic profiles. This was achieved as follows. The electrode was activated with SQW pulses for 2 min at a frequency of 2 Hz from -0.25 to $+1.25$ V vs SCE and the cyclic voltammogram at $60 \mathrm{mV s^{-1}}$ was recorded. The oxide was then removed from the surface with aqua regia and the activation of the oxide-free electrode was carried out potentiodynamically with the same frequency and between the same potential limits as with SQW, until the current of A_2 peak was superimposed with that obtained with SQW polarization.

The frequency dependence of the oxide growth with potentiodynamic and SQW activation is illustrated in Fig. 2, where the current for the oxide formation peak (A_2) taken from a cyclic voltammogram recorded at $60 \mathrm{mV s^{-1}}$ is plotted as a function of cyclic frequency.

Fig. 3 shows potentiostatic polarization curves of a non-activated and a SQW-activated iridium electrode in $0.5 \mathrm{mol dm^{-3}}$ sulphuric acid together with curves measured after a SQW grown oxide

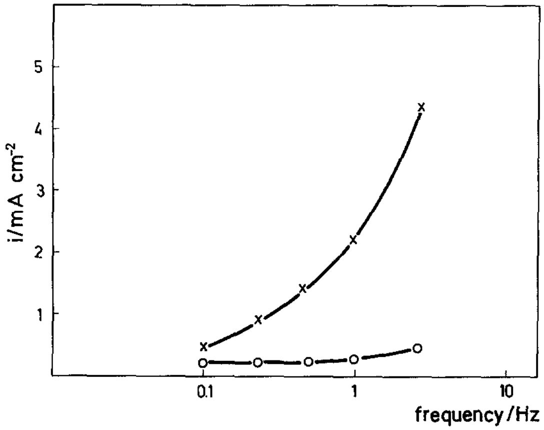

Fig. 2. Rate of activation of iridium electrode expressed as peak height at $+0.75$ V (A_2) of potentiodynamically activated (○) and SQW-activated (x) iridium electrode in $0.5 \mathrm{mol dm^{-3}}$ H_2SO_4 from -0.25 to $+1.25$ V for 2 min.

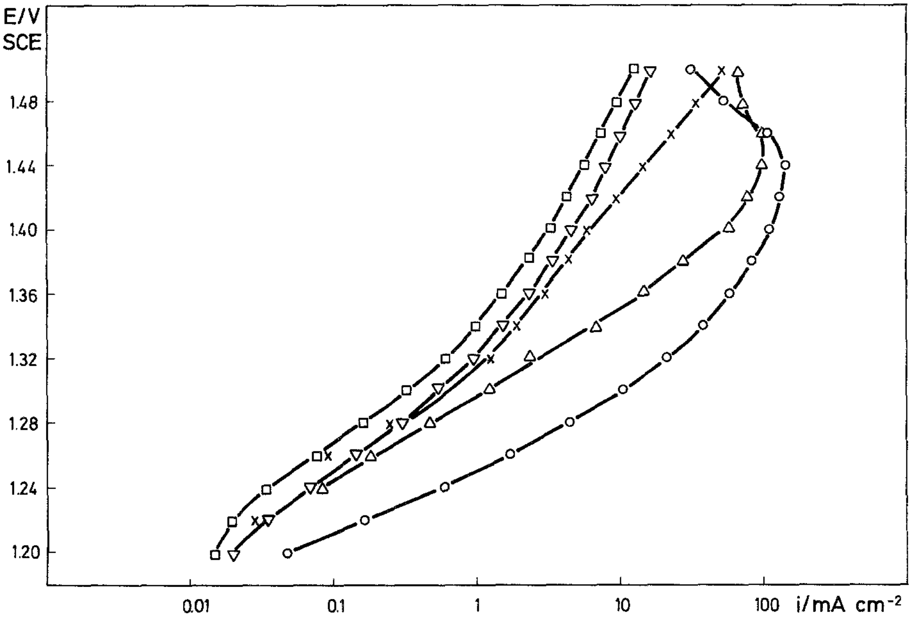

Fig. 3. Potentiostatic polarization of non-activated iridium electrode (□) in O_2-saturated 0.5 mol dm^{-3} H_2SO_4 and SQW-activated (○) electrode for 5 min at 2 Hz from −0.25 to +1.25 V vs SCE, followed by heat treatment for 1 h at 200° C (△), 300° C (x), 400° C(▽).

film was subjected to heat treatment in air for 1 h in the range 200 to 400° C.

Recording Tafel curves on iridium oxide films presents some difficulties. The current varies with time and steady-state conditions are difficult to achieve. To partially overcome this problem it is usual to take the measurements after some time from the beginning of the polarization at each potential. This was also carried out in the present experiments where data in Fig. 3 were taken 3 min after polarization at each potential value. The corresponding Tafel slopes at the low current densities are 40 mV per decade for the activated electrode, increasing to 55 mV per decade after heat treatment at 200° C and reaching 60 mV per decade in the case of the activated electrodes followed by the heat treatment at 300 and 400° C respectively. The same magnitude of Tafel slope of 60 mV per decade has been obtained with the non-activated electrode. There is a break at +1.34 V, and 160 mV per decade was measured at the high current densities on polarization curves of non-activated electrodes and at those treated at 300 and 400° C.

Cyclic voltammograms of thermally treated iridium oxide films exhibit different potentiodynamic profiles in comparison with SQW-activated but thermally non-treated films (Fig. 4). The loss in electrochemical activity of the electrodes is evident. Peaks at +0.75 V as well as those at +1.25 V decrease with firing temperature.

Being aware of the corrosion of iridium during OER it was of interest to compare the stability of the electrode treated at various temperatures during prolonged polarization at anodic potentials. In Fig. 5 the oxygen evolution currents at +1.3 V vs SCE at the bare metal electrode, activated electrode, and at the 200° C thermally treated electrode are plotted as a function of time. Fig. 6 shows polarization data for activated electrodes subsequently heated at 200, 300 and 400° C, respectively.

Fig. 7 shows two cyclic voltammograms before and after an activated and thermally treated (200° C) electrode was polarized for 5 h at +1.3 V. The thermally treated electrode can be further activated either potentiodynamically (Fig. 8) or by SQW (Fig. 9). Fig. 8 shows the

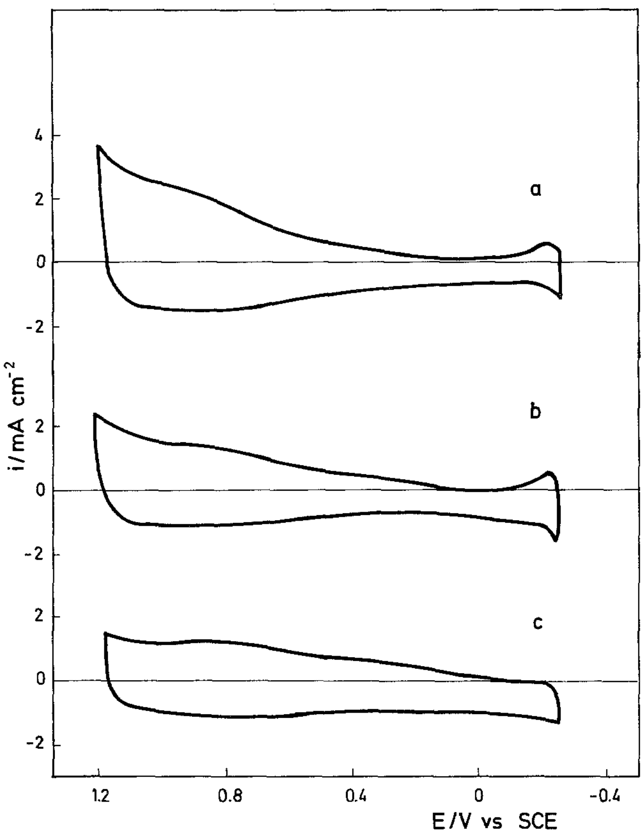

Fig. 4. Cyclic voltammogram at a sweep rate of 60 mV s^{-1} in 0.5 mol dm^{-3} H_2SO_4 for SQW-activated iridium electrode, followed by heat treatment for 1 h at 200° C (a), 300° C (b), 400° C (c).

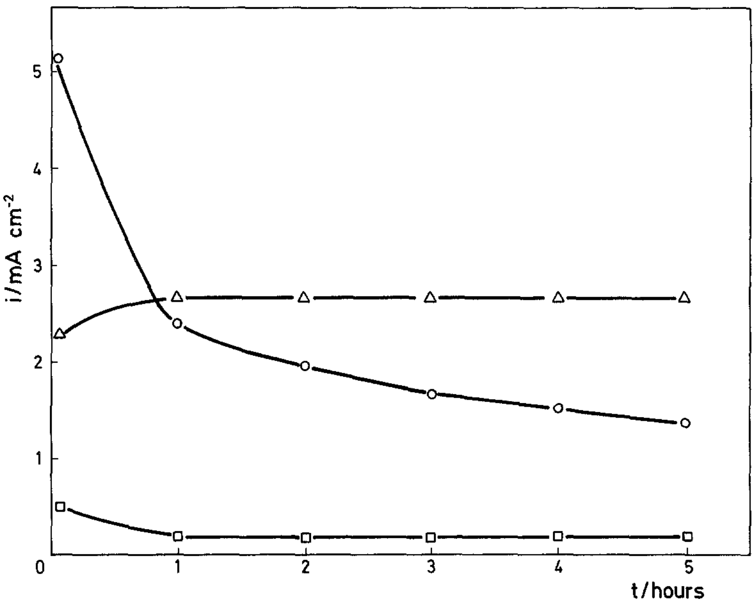

Fig. 5. Potentiostatic polarization at +1.3 V vs SCE in 0.5 mol dm^{-3} H_2SO_4 at 22° C of non-activated iridium electrode (□), SQW-activated for 5 min at 2 Hz from −0.25 to +1.25 V (○) and SQW-activated electrode, followed by heat treatment for 1 h at 200° C (△).

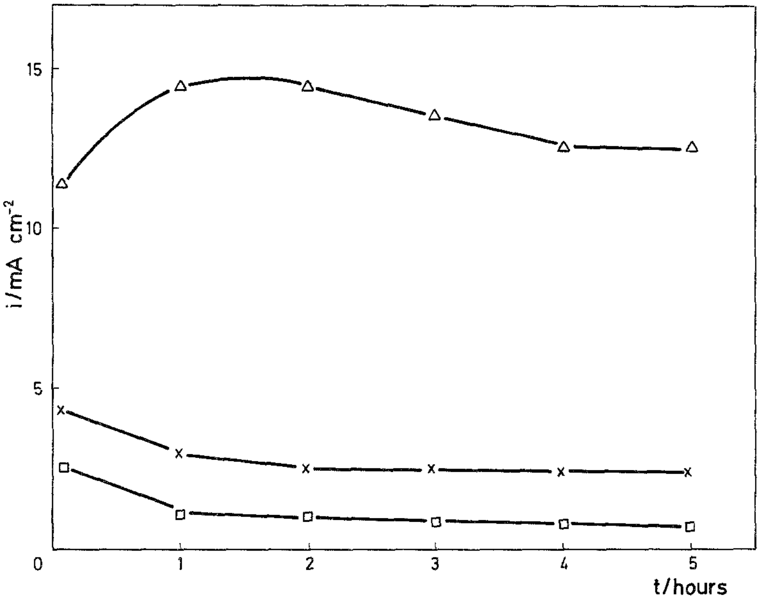

Fig. 6. Potentiostatic polarization at + 1.4 V vs SCE in 0.5 mol dm^{-3} H_2SO_4 at 22° C of SQW-activated iridium electrode, followed by heat treatment for 1 h at 200° C (△), 300° C (x), 400° C (□).

change in the shape of the potentiodynamic profile during cycling; the increase of current at + 1.25 V where oxygen evolution commences is also visible. This is more precisely illustrated in Fig. 10 where the OER current at + 1.3 V of the activated and thermally treated electrode is plotted as a function of number of potentiodynamic cycles from − 0.25 to + 1.25 V at 60 mV s^{-1}. When each sweep was finished at − 0.25 V the potential was switched to + 1.3 V and the current was recorded after 1 min of polarization.

4. Discussion

Previous research work has confirmed that oxide film growth on iridium can be achieved with either repetitive triangular or SQW pulses. In the first part of this work both procedures have been examined. Potential limits were chosen at − 0.25 V and + 1.25 V vs SCE. These limits have been reported as optimal for oxide growth in 0.5 mol dm^{-3} H_2SO_4 [8]. The inspection of cyclic voltammograms in Fig. 1 indicates little differ-

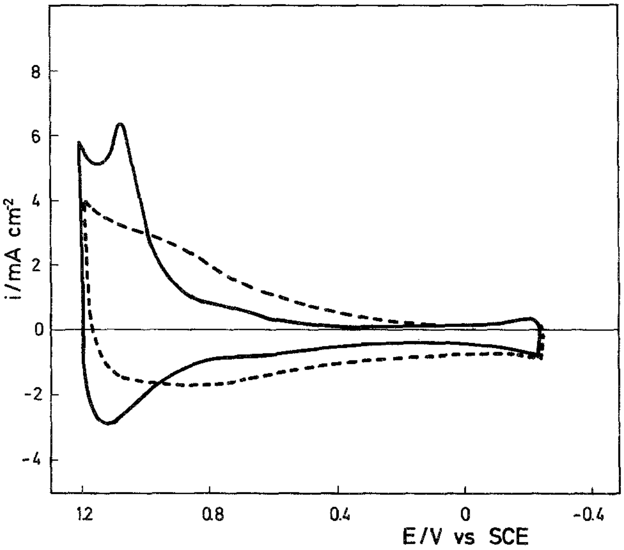

Fig. 7. Cyclic voltammogram at a sweep rate of 60 mV s^{-1} of SQW-activated iridium electrode, followed by heat treatment at 200° C (dashed line) and same electrode after 5 h of polarization at + 1.3 V vs SCE (full line).

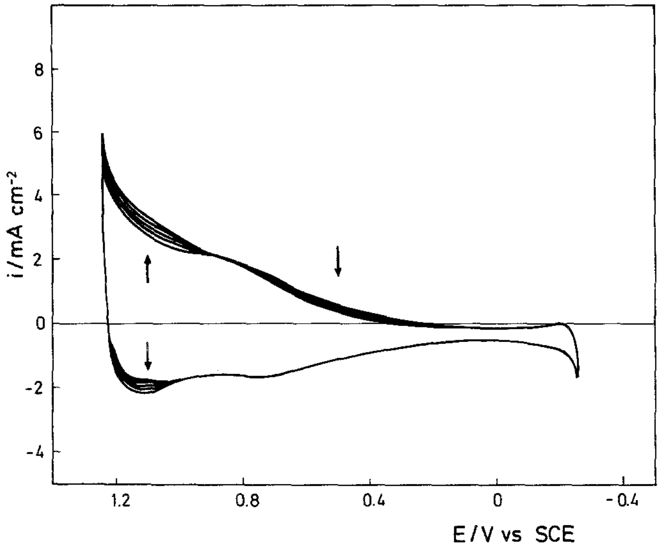

Fig. 8. Cyclic voltammogram at a sweep rate of 60 mV s^{-1} of SQW-activated iridium electrode, followed by heat treatment at 200° C. The arrows denote direction of current during cycling.

ences between the two procedures. Both cyclic voltammograms are characterized by three oxidation peaks, A_1, A_2 and A_3, and two reduction peaks, C_2 and C_3, respectively. Only the shoulder at + 0.6 V (A_1) and oxide formation and reduction peaks at + 1.15 V (A_3 and C_3) were more developed after SQW polarization. However, square wave activation was much faster. It took 55 min with potentiodynamic polarization in comparison with 2 min with SQW to obtain the same oxide thickness. This phenomenon of faster SQW activation was also observed by Gottesfeld and McIntyre [8]. Buckley *et al.* [17] have measured the dependence of oxide growth on cycling frequency and on the cathodic and anodic limits of polarization. The present results confirm their findings that only repetitive polarization at high anodic and cathodic potentials is responsible for oxide growth and electrode activation.

The fact that thick oxide film on iridium is a better electrocatalyst than bare metal is illustrated in Fig. 3, where it is shown that an approximately 30-fold increase in current at the

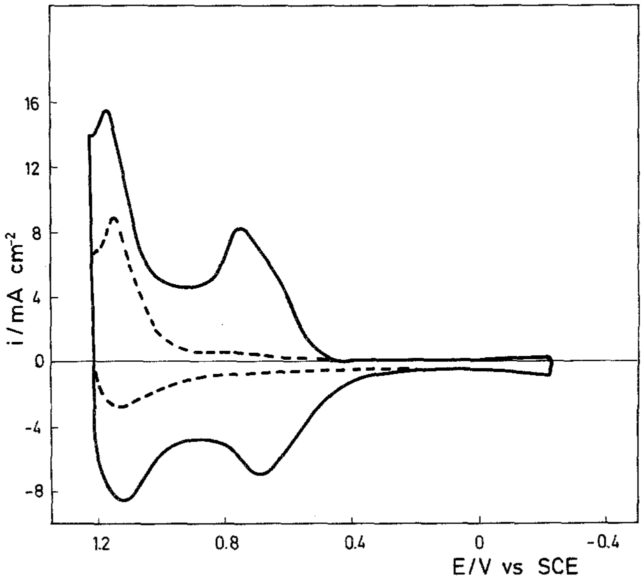

Fig. 9. Cyclic voltammograms of SQW-activated iridium electrode, followed by heat treatment at 200° C and 5 h of polarization at + 1.3 V vs SCE (dashed line). This electrode was subjected to further SQW activation for 5 min at 2 Hz from − 0.25 to + 1.25 V vs SCE (full line).

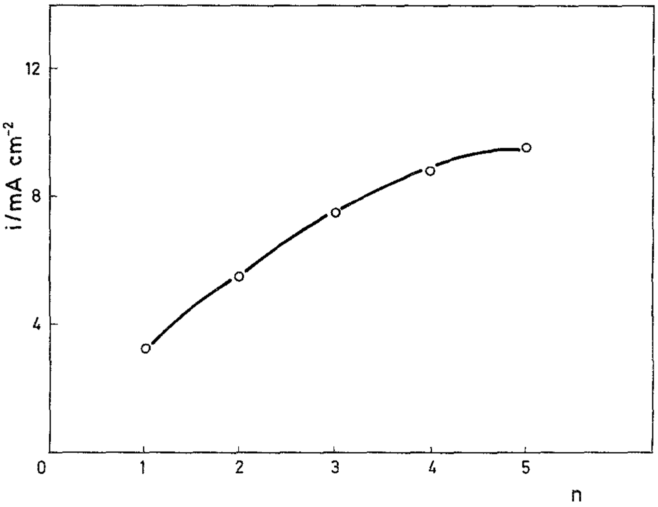

Fig. 10. OER current at +1.3 V of SQW-activated electrode, followed by heat treatment at 200° C versus number of potentiodynamic sweeps at 60 mV s^{-1} from −0.25 to +1.25 V vs SCE (cf. Fig. 8). Data were taken 1 min after the potential was switched to +1.3 V.

same potential is obtained at the activated electrode. This electrode also exhibits a lower Tafel slope of 40 mV per decade in comparison with the 60 mV per decade of the bare metal electrode, results which are similar to those obtained by Gottesfeld and Srinvasan [31] where enhanced electrode activity and a decrease in the Tafel slope of the OER have been observed on the electrolytically grown oxide film on iridium. The break in Tafel slope at about +1.34 V, also reported previously in the case of a non-activated electrode [31, 37], indicates the change in the mechanism of the OER. Further investigation of the dependence of OER current on oxide thickness was not examined in this work. Frazer and Woods [35] reported an increase of the OER current with the amount of oxide present. What is also significant in the case of the activated electrode is the decrease in the current at potentials above +1.44 V due to corrosion of iridium which, according to Kötz *et al.* [39] proceeds by oxidation or iridium to the hexavalent state and dissolution as the IrO_4^{2-} ion. Relating to this phenomenon an attempt was made to stabilize the oxide film by thermal treatment. The oxide film formed by SQW pulses at 2 Hz for 5 min was subjected to heat treatment in air between 200 and 400° C. This treatment caused a decrease in OER current at high anodic potentials at electrodes heated at 300 and 400° C, respectively. Corresponding cyclic voltammograms (Fig. 4) show the loss in electrochemical activity. A hydrous oxide film of a thermally non-treated electrode with its open structure, where water and electrolyte species are trapped, was suggested by Burke and O'Sullivan [36] as three-dimensional electrocatalyst for the OER. Thermal treatment obviously changes the properties of such a hydrous type of oxide which becomes anhydrous, more compact and with lower surface area. Its cyclic voltammograms after thermal treatment at various temperatures (Fig. 4) are quite different in comparison with a cyclic voltammogram of thermally non-treated electrodes (Fig. 1) and in fact are more similar to those obtained by Ardizzone *et al.* [15] using IrO_2 formed by thermal decomposition of $IrCl_3$. In their experiments the voltammetric charge also decreases with firing temperature.

During the oxygen evolution reaction the non-activated iridium electrode, the activated electrode and the activated electrode which was subjected to thermal treatment, exhibit different electrocatalytic activity (Figs 5, 6). The non-activated electrode exhibits decrease in the OER current during the first hour of polarization and stable current for the rest of the experiment (Fig. 5). The initial decay of the OER current on iridium at the beginning of polarization was also detected by Buckley and Burke [33], the slope of decay varying with anodic potential. The activated electrode also shows high current at the very beginning of the electrolysis (Fig. 5) and a sharp decay immediately after polarization was started. Such a phenomenon was also observed by Gottesfeld and Srinivasan [31] for this type of electrode, and Beni and co-workers [41, 42] who were able to produce a stable iridium surface during OER using sputtered iridium oxide films.

In this paper we report that stabilization of the iridium oxide surface can be achieved by heat treatment of the oxide film. As can be seen in Fig. 5 when the SQW-activated electrode is heated for 1 h at 200° C stabilization of the surface takes place. At the beginning of the electrolysis the electrode is less active in comparison with a thermally non-treated electrode, but there is a significant difference in their behaviour during continuous polarization. The OER current at the activated, but thermally non-treated, electrode decreases continuously with time, while the current at the thermally treated electrode increases during the first hour of polarization and is stable afterwards. This electrode was examined before and after polarization and the cyclic voltammogram (Fig. 7) shows a shift of voltammetric charge towards more positive potentials in the voltammogram recorded after 5 h of polarization. The explanation for such a voltammetric profile is a change in the stoichiometry of the iridium oxide to a higher oxidation state of iridium, its surface becoming more efficient for the adsorption of OH^- intermediates taking part in the OER. This supports the conclusion drawn by Gottesfeld and Srinivasan [31] where the change in stoichiometry of iridium is responsible for the better electrocatalytic activity in the OER of the cycled iridium electrode in acid solution. Similar effects have been obtained with an activated rhodium electrode in base [43] and ruthenium in acid [44] where cycling of the electrode also produced a change in oxide stoichiometry. It was shown also by Iwakura *et al.* [45] that an anhydrous ruthenium dioxide electrode subjected to thermal treatment exhibits a more stable surface during anodic polarization in perchloric acid. The fact that thermally treated iridium oxide films are also sensitive to further activation (Figs 8, 9) and rather significant changes in the OER current after only a few cycles of potentiodynamic activation (Fig. 10) clearly indicates that the intrinsic properties of the oxide layer play a dominant role in the electrocatalysis of the oxygen evolution reaction.

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References

[1] S. Trasatti and G. Lodi, in 'Electrodes of Conductive Metallic Oxides', part B (edited by S. Trasatti), Elsevier, Amsterdam (1981) p. 521.
[2] L. D. Burke, *ibid.* p. 141.
[3] M. R. Tarasevich, A. Sadkowski and E. Yeager, in 'Comprehensive Treatise of Electrochemistry, Vol. 7' (edited by B. E. Conway, J. O'M. Bockris, E. Yeager, S. U. M. Khan and R. E. White), Plenum Press, New York (1983) p. 301.
[4] S. Trasatti, *Electrochim Acta* **29** (1984) 1503.
[5] J. O'M. Bockris and T. Otagawa, *J. Phys. Chem.* **87** (1983) 2960.
[6] S. Gottesfeld, J. D. E. McIntyre, G. Beni and J. L. Shay, *Appl. Phys. Lett.* **33** (1978) 208.
[7] G. Beni and J. L. Shay, *ibid.* **33** (1978) 567.
[8] S. Gottesfeld and J. D. E. McIntyre, *J. Electrochem. Soc.* **126** (1979) 742.
[9] P. Stonehart, H. Angerstein-Kozlowska and B. E. Conway, *Proc. Roy. Soc., A* **310** (1969) 541.
[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] J. M. Otten and W. Visscher, *ibid.* **55** (1974) 1.
[13] *Idem, ibid.* **55** (1974) 13.
[14] A. T. Kuhn and C. J. Mortimer, *J. Electrochem. Soc.* **120** (1973) 231.
[15] S. Ardizzone, A. Carugati and S. Trasatti, *J. Electroanal. Chem.* **126** (1981) 287.
[16] D. N. Buckley and L. D. Burke, *J. Chem. Soc. Faraday Trans* **71** (1975) 1447.
[17] D. N. Buckley, L. D. Burke and J. K. Mulcahy, *ibid.* **72** (1976) 1896.
[18] L. D. Burke and D. P. Whelan, *J. Electroanal. Chem.* **162** (1984) 121.
[19] D. Michell, D. A. J. Rand and R. Woods, *ibid.* **84** (1977) 117.
[20] J. O. Zerbino, N. R. de Tacconi and A. J. Arvia, *J. Electrochem. Soc.* **125** (1978) 1266.
[21] J. O. Zerbino and A. J. Arvia, *ibid.* **126** (1979) 93.
[22] L. D. Burke and D. P. Whelan, *J. Electroanal. Chem.* **124** (1981) 333.
[23] S. H. Glarum and J. H. Marshall, *J. Electrochem. Soc.* **127** (1980) 1467.
[24] J. Mozota and B. E. Conway, *Electrochim. Acta* **28** (1983) 1.
[25] *Idem, ibid.* **28** (1983) 9.
[26] V. Birss, R. Myers, H. Angerstein-Kozlowska and B. E. Conway, *J. Electrochem. Soc.* **131** (1984) 1502.
[27] H. Y. Hall and P. M. A. Sherwood, *J. Chem. Soc. Faraday Trans. I* **80** (1984) 135.
[28] M. Peuckert, *Surface Sci.* **144** (1984) 451.

[29] J. Augustynski, M. Koudelka, J. Sanchez and B. E. Conway, *J. Electroanal. Chem.* **160** (1984) 233.

[30] M. Pueckert, *ibid.* **185** (1985) 379.

[31] S. Gottesfeld and S. Srinivasan, *ibid.* **86** (1978) 89.

[32] A. Damjanović and M. K. Y. Wang, *J. Electrochem. Soc.* **114** (1967) 592.

[33] D. N. Buckley and L. D. Burke, *J. Chem. Soc. Faraday Trans. 1* **72** (1976) 2431.

[34] M. H. Miles, E. A. Klaus, B. P. Gunn, J. R. Locker, W. E. Serafin and S. Srinivasan, *Electrochim. Acta* **23** (1978) 521.

[35] E. J. Frazer and R. Woods, *J. Electroanal. Chem.* **102** (1979) 127.

[36] L. D. Burke and E. J. M. O'Sullivan, *ibid.* **117** (1981) 155.

[37] A. Damjanović, A. Dey and J. O'M. Bockris, *J. Electrochem. Soc.* **113** (1966) 739.

[38] J. O'M. Bockris, *J. Chem. Phys.* **24** (1956) 817.

[39] R. Kötz, H. Neff and S. Stucki, *J. Electrochem Soc.* **131** (1984) 72.

[40] R. Kötz, H. J. Lewerenz, P. Brüesch and S. Stucki, *J. Electroanal. Chem.* **150** (1983) 209.

[41] G. Beni, L. M. Schiavone, J. L. Shay, W. C. Dautremont-Smith and B. S. Schneider, *Nature* **282** (1979) 281.

[42] S. Hackwood, L. M. Schiavone, W. C. Dautremont-Smith and G. Beni, *J. Electrochem. Soc.* **128** (1981) 2569.

[43] L. D. Burke and E. J. M. O'Sullivan, *J. Electroanal. Chem.* **93** (1978) 11.

[44] M. Vuković, H. Angerstein-Kozlowska and B. E. Conway, *J. Appl. Electrochem.* **12** (1982) 193.

[45] C. Iwakura, K. Hirao and H. Tamura, *Electrochim. Acta* **22** (1977) 335.