Reversible ageing of iridium oxide electrodes in acidic solutions

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The cyclic voltammetric response of iridium oxide films, grown electrochemically in acidic solutions, can display a notable dependence on the time spent in the reduced state and on other factors such as the carrying out of very slow sweep rate experiments. This is seen primarily as a substantial positive shift of the anodic peaks and in a diminishment, by up to about 50%, in the reaction kinetics. This effect, termed as film ageing, can be reversed, either by long times of cycling over an extended range of potential or by a brief holding period in the oxidized state of the film. Oxide films do not exhibit ageing in alkaline solutions. It is, therefore, suggested that film ageing is associated primarily with the loss of water from the film in acidic solutions at negative potentials, resulting in the inhibition of subsequent ion/solvent transport processes in the film.

1. Introduction

There has been a great deal of interest in the electrochemical behaviour of iridium oxide electrodes for a number of years [1-26]. This has stemmed both from its interesting electrochemistry and also due to its numerous potential practical applications, for example in display devices (due to its electrochromic properties [4, 5]), as a neural stimulating electrode [25, 26], and also because of its potential as a cathode for advanced rechargeable batteries. For all of these purposes, it is desirable that the oxide film be chemically/physically stable and that it displays rapid and reproducible oxidation/reduction kinetics.

A detailed study by Mozota and Conway [7, 8] formed part of the pioneering investigations of electrochemically formed iridium oxide films. The main redox peaks, A1/C1, were attributed to the Ir(III)/(IV) redox process and the prepeak, A0, was linked to the presence of anions in the oxide film. Further studies by Burke et al. [10-12] and later by Pickup and Birss [14-18] showed that electrochemically grown Ir oxide films display a greater than 60mV pH dependence over a wide range of pH, consistent with earlier reports [1]. Based on the chemical analysis of the contents of the oxide film in the oxidized and reduced states, in both acidic (HX) and alkaline (MOH) solutions [16], and on in situ mass measurements [24], the following reactions have been shown to describe iridium oxide electrochemistry in aqueous solutions:

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\begin{align*}
(M^+)_3[Ir_5O_{16}(OH)_73H_2O]^{2-} + 5e^- + 7H_2O & \leftrightarrow (M^+)[Ir_5O_{10}(OH)_{10}H_2O]^+ + 2M^+ + 7OH^- \\
(IrO_2nH_2O)_5 + 5e^- + 7H_3O^+ + 2X^- & \leftrightarrow [Ir_5O_{10}(OH)\_75H_2O]^{2+}(X^-)_2 + 7H_2O
\end{align*}
\]

In the present work, we have focussed primarily on elucidating some of the factors which are responsible for the instability of the iridium oxide electrochemical response, when particular solutions, electrochemical growth conditions and potentials are employed. Similar to prior references [6, 10, 18], this will be referred to as film ageing phenomena, which can be either reversible or irreversible in nature in the case of iridium oxide electrodes. Importantly, both forms of ageing significantly influence the kinetics of the principal redox reaction. In this paper, the conditions which provoke iridium oxide ageing will be examined and an effort will be made to explain it in terms of structural/compositional changes which occur within the oxide film in relation to Reactions 1 and 2. It is of interest that similar results to those shown here have recently been reported for a number of polymer modified electrodes, e.g. polyaniline, Nation, etc. [27-32]. Also, analogous effects have been reported for oxides formed electrochemically at amorphous alloy electrodes [33].

2. Experimental details

2.1. Equipment, cells and chemicals

An EG&G PARC 173 potentiostat was used with a PARC 175 universal programmer and a PARC 179 digital coulometer. Voltammograms were

* This paper is dedicated to Professor Brian E. Conway on the occasion of his 65th birthday and in recognition of his outstanding contribution to electrochemistry.

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recorded on a Hewlett-Packard 7044A or a BBC SE780 X–Y recorder, while current and charge transients were collected and displayed by an HP7090 digital plotter. All electrochemical experiments were carried out in conventional three-compartment glass cells, under argon at room temperature. All reagents were Fisher certified or Reagent ACS grade and were used as received, and all water was triply distilled.

2.2. Electrodes

Working electrodes were constructed from glass-mounted iridium wire (99.9%, Johnson Matthey, 0.5 mm diam.). All electrode areas referred to in this paper are geometric areas (about 0.1 cm²). All potentials are quoted relative to the saturated sodium calomel electrode (SSCE, +236 mV vs SHE) which was separated from the working electrode by a Luggin probe. The counter electrode was a large area platinum gauze located in a separate compartment.

2.3. Electrode pretreatment and oxide growth

Before oxide growth, the electrode was generally cleaned electrochemically [14] by holding the potential at 2 V vs SSCE in 10% H₂SO₄ for about 5 min. Another rapid and efficient cleaning method, not used previously by us for iridium oxide electrodes, involved placing the electrode into the reducing part of a natural gas/air flame for several seconds. To grow an iridium oxide film, the potential was cycled (1 V s⁻¹) or pulsed at 1 s intervals between 0.24 and 1.31 V in sulphuric and nitric acid solutions. Depending on the desired thickness of the oxide film, the time of potential cycling/pulsing was varied from a few minutes up to about 1 h.

2.4. Determination of quantity of hydrous iridium oxide

The amount of Ir oxide film formed was assessed by measuring the charge passed in a slow sweep CV experiment [14–18] between particular potential limits. Slow potential sweeps are essential in order to achieve equilibrium within the oxide film, so that all of the iridium sites have time to react. For thick oxide films, scan rates in the range of 1 to 20 mV s⁻¹ were required for charge measurement, while in the case of thin oxides, higher sweep rates of up to 100 mV s⁻¹ could be used. The positive potential limit (E⁺) used for charge calculations was 1.0 V [15] in both 0.5 M H₂SO₄ and 1 M HNO₃ solutions. The charges, which are considered to be proportional to the oxide film thickness, are represented by a charge enhancement factor (CEF) [7–9, 14, 15], considered to be a measure of the number of monolayers of iridium oxide film present. The CEF is equivalent to the ratio of the oxide charge density after a particular growth period to the charge in the first scan of potential at a fresh iridium electrode (about 0.11 mC cm⁻² [15]). Iridium oxide films characterized by CEF values in the ranges of 40–80, 80–280, 280–500 and beyond 500 are classified in this work as thin, medium, thick and very thick, respectively. Based on our previous work [15], a CEF of unity was shown by SEM studies to be equivalent to a dry film thickness of about 15 Å.

![Cyclic voltammetric response](image_url)

Fig. 1. Cyclic voltammetric response, 100 mV s⁻¹, of thick (CEF = 282, ——) and thin (CEF = 61, ———) iridium oxide film in 0.5 M H₂SO₄ with continuous cycling of potential after oxide growth and potential holding at −0.24 V for 5 min. Cycle numbers after holding are shown on the CVs.