ELSEVIER

Voltammetry and impedance measurements of Ir(1 1 1) electrodes in aqueous solutions

T. Pajkossy *, L.A. Kibler, D.M. Kolb

Department of Electrochemistry, University of Ulm, D-89069 Ulm, Germany

Dedicated to Ron Fawcett on the occasion of his 65th birthday and his contribution to electrochemistry

Abstract

The electrochemical behaviour of Ir(1 1 1) electrodes has been studied in simple aqueous solutions, in the presence and absence of various adsorbates: sulphate, phosphate and halide anions. In general, this electrode is very similar to Pt(1 1 1); however, the rates and relative strengths of adsorption are different. In the accessible potential range no capacitance peak similar to that of Pt(1 1 1) was found, and no Gouy–Chapman minimum could be identified. CO adlayer stripping from Ir(1 1 1) in sulphuric acid occurs in the same potential region as for Pt(1 1 1).
© 2005 Published by Elsevier B.V.

1. Introduction

The platinum group metals play an important role in electrochemistry, not only for their relevance in practical applications, but also because of their unique properties, viz. they are noble metals but their surfaces are very reactive. Platinum is the most active metal for many reactions and has been widely studied mostly with single crystal electrodes having highly reproducible, well-defined surfaces. Especially Pt(1 1 1) has been intensively studied in the past two decades; these studies have recently been surveyed in [1]. Electrochemical studies on single crystals of platinum and other members of the platinum group, including the reactive ones, have also been performed in our laboratory [2–4]; the present

study with Ir(1 1 1) electrode is a continuation of these efforts.

Iridium, being a neighbour of Pt in the periodic system of elements, is very similar to Pt when their physical and chemical properties are considered. Hence, very similar electrochemical behaviour of their (1 1 1) single crystal faces can be expected. We note that in all previous studies of Ir single crystals [5–7] the results are in accord with these expectations.

The aim of the present work is to explore various basic aspects of the Ir(1 1 1) electrode in aqueous solutions: we concentrate on voltammetric and impedance behaviour to obtain information on the electric double layer and on anion as well as hydrogen adsorption on this electrode.

2. Experimental

The experimental set-up (instruments and software for cyclic voltammetry, impedance/capacitance

---

* Corresponding author. Permanent address: Institute of Materials and Environmental Chemistry, Chemical Research Center, Hungarian Academy of Sciences, Budapest, Pusztaszeri út 59-67, H-1025, Hungary. Tel.: +36 13257900; fax: +36 13257892.
   E-mail address: pajkossy@chemres.hu (T. Pajkossy).

measurements), the cell, chemicals, and all the experimental procedures, e.g., how the impedance measurements are analyzed, have already been described in an earlier publication [8]. Ir(1 1 1) (MaTecK GmbH, Jülich, Germany) requires a high temperature annealing ($T > 1500\ °C$) [6]. The crystal (4 mm in diameter) was annealed at about $1900\ °C$ in a quartz tube, in a $N_2 + H_2$ gas stream for 100 s, the energy being provided by an induction coil and its power supply (Himmelwerk 2000, Tübingen, Germany); the annealing temperature was checked by an Impac ISR-12-Lo pyrometer. After annealing, the crystal was transferred to the electrochemical cell under 5N argon or in a 6N nitrogen stream, where a hanging meniscus configuration was formed.

In this communication, all measured and fitted (simulated) spectra are represented graphically by plotting $C(\omega) = Y(\omega)/(i\omega) = 1/([Z(\omega) - Z(\omega \to \infty)]A_e i\omega)$ in the complex plane representation. In this equation ω, $Z(\omega \to \infty) = R_s$ and A_e are the angular frequency, the solution resistance and the electrode area, respectively. All the spectra shown in this paper comprise nine points per frequency decade, with the 10 Hz data point marked.

3. Results and discussion

In order to characterize the general electrochemical behaviour of the Ir(1 1 1) electrode, voltammetry and impedance measurements were carried out in simple aqueous electrolytes as described in the following.

The voltammogram in perchloric acid solution is shown in Fig. 1(a). It is fairly similar to that published recently by Gómez and Weaver [7]; one can see hydrogen and hydroxide adsorption regions separated by a double-layer charging region, like in the case of Pt(1 1 1) in that solution. Three differences are, however, to be stressed: First, the characteristic peak in the OH^- adsorption region is less sharp than in the case of Pt(1 1 1); second, the voltammogram is not symmetrical to the potential axis, indicating that the hydrogen and hydroxide adsorption is slower than on Pt(1 1 1), and third, the double-layer region is about twice as wide. With increasing pH the voltammogram shifts by about -0.06 V/pH; however, the overall shapes of the voltammograms are similar to each other. This is true for acidic (pH < 4) solutions, in which adsorption or desorption of H^+ ions cannot cause local pH changes.

In contrast, with unbuffered neutral or close-to-neutral solutions the shape of the voltammograms is strongly affected by the local pH changes closeby the interface, as it will be shown and discussed below. In alkaline solutions (pH > 10) the shape of the voltammograms is again dominated by the hydrogen and hydroxide adsorption regions separated by the double-layer
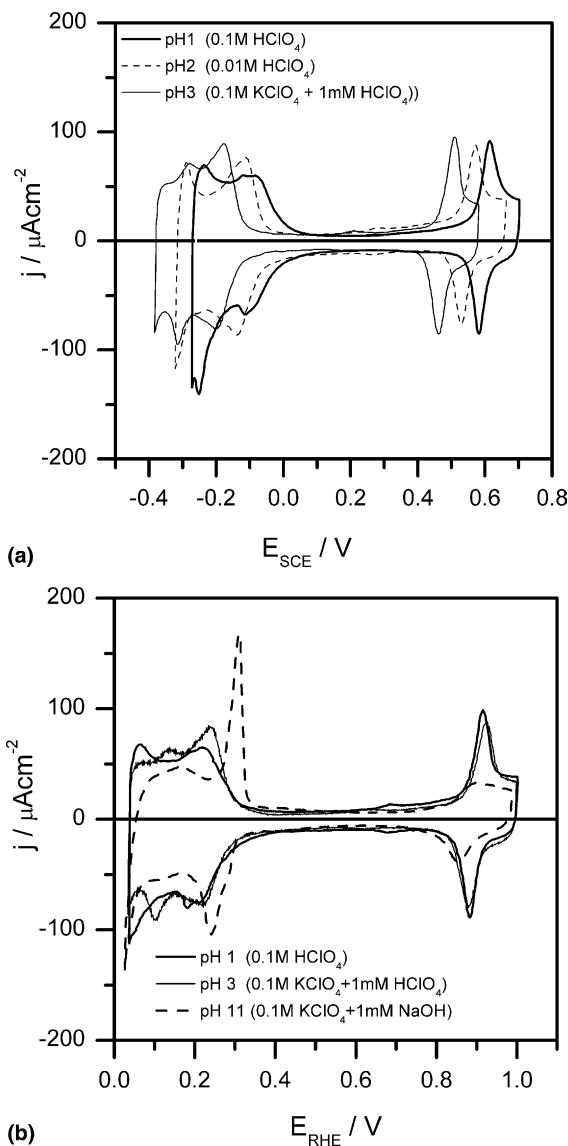

Fig. 1. Voltammograms of Ir(1 1 1) at 50 mV/s as function of pH of perchlorate solutions: (a) in x M $HClO_4 + y$ M $KClO_4$, plotted on a SCE potential scale; (b) re-plotted on the RHE scale. For comparison, a voltammogram taken in an alkaline solution (1 mM NaOH + 0.1 M $KClO_4$, pH 11) is also shown.

region. However, in alkaline solutions a pronounced peak appears at the positive end of the hydrogen adsorption region, the nature of which is not clear yet. In general, the hydrogen and hydroxide adsorption regions appear at the same potentials on the reversible hydrogen electrode (RHE) scale (Fig. 1(b)).

The total charge associated with the hydrogen adsorption region is about 0.26 mC/cm^2, which, taking into account the various sources of uncertainties, is in good agreement with the charge of a hydrogen monolayer on Ir(1 1 1), $252\ \mu C/cm^2$ [6]. The hydroxide adsorption peak bears about one-third of this charge.

In the hydrogen adsorption region the adsorption equilibria can be described as