THE OXYGEN AND HYDROGEN EVOLUTION REACTION ON ORIENTED SINGLE CRYSTALS OF RUTHENIUM DIOXIDE*

L.I. Bergar, Fred H. Pollak and Y. Canivez[a)]
Department of Physics
Brooklyn College of CUNY
Brooklyn, N.Y. 11210

and

W. O'Grady
Department of Energy and Enrironment
Brookhaven National Laboratory
Upton, N. Y. 11973

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Abstract

A novel design for water electrolysis using a solid polymer electrolyte is being developed by General Electric. Ruthenium is one of the best electrocatalysts for the oxygen evolution reaction. There are problems connected with the significant loss in electrocatalytic activity with time. This performance degradation is presumably due to the gradual formation of an RuO_2 film.

We have performed electrochemical measurements on [100], [110] and [111] oriented single crystals of RuO_2 in order to elucidate the mechanism of the electrocatalytic process. Large single crystals were grown by the vapor transport method. Our investigation has revealed several interesting differences for the various orientations. This study indicates that RuO_3 may be an important intermediate species prior to oxygen evolution and that the formation of the RuO_3 is the rate limiting process. Similar results were previously obtained for IrO_2.

I. Introduction

At the present time there is considerable interest in developing high efficiency and low cost water electrolyzers to meet the demands of hydrogen required by the chemical industry and as a fuel in fuel cells and gas turbines. The development of advanced technology for water electrolysis is essential to minimize the cost of hydrogen. The efficiency of water electrolysis systems depends critically on the behavior of the oxygen electrode. For oxygen evolution reaction (OER) on metals or alloys at constant potentials, the continuous decrease of current densities with time is one of the more difficult problems in water electrolysis. The time variation of current density has been pointed out by Schultze[1] in the anodic evolution of oxygen on platinum. More recently, similar behavior has been observed on iridium[2] and on nickel[3] anodes. It has been suggested that the current decay with time is connected with the continuous growth of a poorly conducting oxide film, which retards the electron transfer or inhibits the radical on the film surfaces[2,3,4]. Based on electrochemical and ellipsometric methods Srinivasan et al have concluded that the performance degradation for oxygen evolution on RuO_x catalyst is presumably due to the gradual accumulation of a RuO_2 film on the surface of the RuO_x particles by a dissolution/precipitation process.[4]

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a) Permanent address: Faculte des Sciences, University of Mons, Mons, Belgium.

The OER always takes place on electrodes which are covered with an oxide layer. Little is understood about the properties of the oxide phase and, especially, about the properties of the oxide-electrolyte interface which are required to achieve improved performance in the OER, Evaluation of a number of metals and alloys as electrocatalysts for the oxygen evolution reaction, leads to nickel as a preferred anode material for the OER in alkaline solutions and to noble metals and their alloys as electrocatalysts for the OER in acid solutions. Among the noble metals, the performance of Ru, Ir and their alloys was found to be much superior to that of a pure Pt anode. Thus, the potential at which a steady state oxygen evolution current density of 1 mA cm^{-2} (real) is obtained on Pt at room temperature is about 1.8 V vs. RHE, while at a Ru or an Ir anode this potential is only about 1.4V (Ru) or 1.5V (Ir).[5,6] It is obvious, therefore, that analysis of the surface layer formed on Ru or Ir prior and during the evolution of oxygen, revealing the relationship between properties of this layer and the performance of the Ru (Ir)/ aqueous solution interface in the OER, may be an important key to the role of oxide layers in electrocatalysis. In addition the work of Srinivasan et al[4] has shown the significance of our understanding the properties of RuO_2 and IrO_2.

A novel design for water electrolysis is being developed by the General Electric Company using solid polymer electrolytes.[7] In this type of water electrolysis cell a solid sheet of perfluorinated polymer (Nafion) serves as the electrolyte. The electrocatalysts are platinum on the cathode side and iridium, ruthenium or binary and ternary alloys of these metals with transition metals on the anode side. Hence there is considerable interest from a practical point of view in gaining a better understanding of nature of electrocatalyst/electrolyte interface for these particular materials.

II. Experimental Results

We have performed cyclic voltammetry and steady state measurements on oriented single crystals of RuO_2. For comparison we have also studied unoriented single crystals of this material and as well as Ru metal. In the single crystal case [100] [110] and [111] crystallographic faces were investigated. This work on oriented single crystal material offers the advantage of a more clearly defined electronic mechanism compared to prior studies on multicrystalline material.[8,9] Fine grained material has many grain boundaries and in some cases inclusions containing impurities. It is also an important continuation of the work on single crystal IrO_2 reported at last year's meeting.[10]

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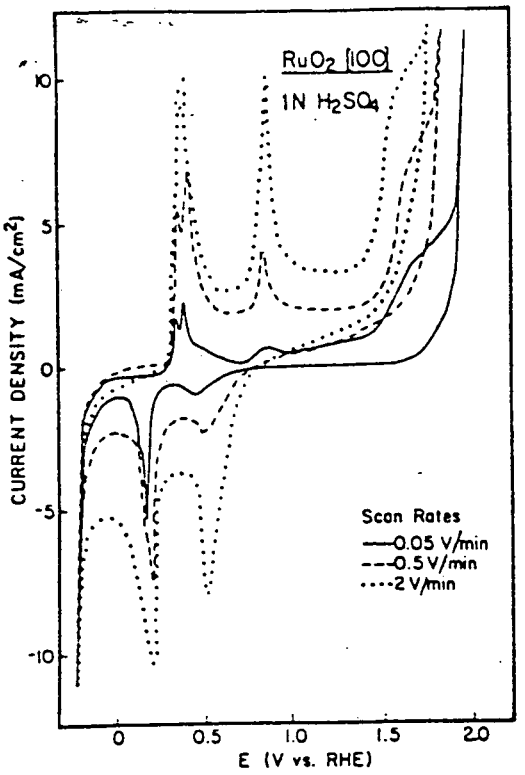

Figure 1. Cyclic voltammetry of single crystal RuO_2 with a [100] surface in a N_2 saturated solution of 1 N H_2SO_4 for several different scan rates.

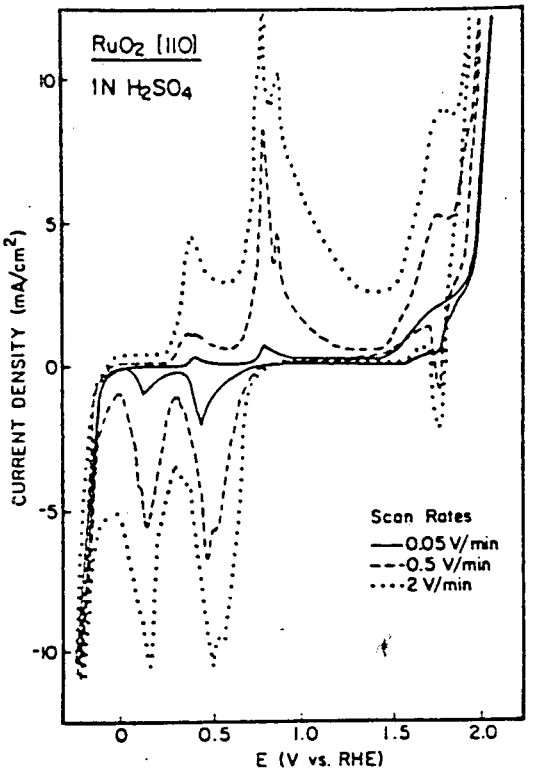

Figure 2. Cyclic voltammetry of single crystal RuO_2 with a [110] surface in a N_2 saturated solution of 1 N H_2SO_4 for several different scan rates.

Single crystals of RuO_2 were grown in our laboratory by the method of chemical transport reactions in a flowing system. This technique is similar to that used by Reames[11] to produce the large single crystals of IrO_2 that were used in our investigation reported at last year's meeting.[10] In the presence of oxygen at 800–1500°C gaseous oxides (RuO_3, IrO_3) exist. The reaction takes place by the following mechanism:

$$M(s) + \frac{3}{2}O_2 \longrightarrow MO_3(g)$$

where M = Ru or Ir. The volatile MO_3 gas dissociates to MO_2 in the cooler region. In our procedure several grams of Ru metal powder were contained in an alumina source boat. This boat was placed inside a Mullite tube at the center of furnace which was raised to a temperature of 1400°C. Oxygen at atmospheric pressure was passed through the Mullite tube at a flow rate of about 15 cm^3/min. A second boat, which acted as a substrate, was placed 210 cm from the source boat in a cooler portion of the furnace. After several days crystals of dimensions up to 6mm x 4mm x 2mm had formed in the substrate boat. Recently Shafer et al have also reported the growth of comparable sized single crystals of RuO_2.[12]

A number of crystals were examined by X-ray Laue backscattering which indicated that they were of relatively good quality. Using the X-ray orientation technique natural [100], [110] and [111] faces were found for the electrochemical investigation.

Shown in Figures 1, 2 and 3 are cyclic voltammograms for [100], [110] and [111] surfaces of RuO_2, respectively, in a 1 N solution of H_2SO_4 saturated with N_2 at different scan rates. Figure 4 shows the results of a similar investigation on an unoriented single crystal. Measurements were actually prtformed at scan rates of 0.05, 0.1, 0.2, 0.5, 1.0 and 2.0 V/min. but for convenience only three rates (0.05, 0.5 and 2.0 V/min.) are displayed. Below about 1.5 V vs RHE the four curves are qualitatively similar with major features at 0.4 and 0.7 V vs RHE on the anodic portion and at about 0.5 and 0.2 V vs RHE in the cathodic region. The potentials of these features are independent of sweep rate.

For the [100] case (see Figure 1) the first anodic peak (0.4 V vs RHE) consists of a well-defined doublet and there is some structure on the cathodic peak at 0.2 V vs RHE. For the [110] crystallographic face (see Figure 2) the second anodic peak (0.75 V vs RHE) is a doublet and there is structure on both cathodic peaks. The [111] face (see Figure 3) shows no structure on either the anodic or cathodic peaks at voltages below ~ 1.5 V vs RHE. Is is of interest to note that the two anodic peaks are at the same voltage for the three orientations while there are small differences (~ 0.1 V vs RHE)

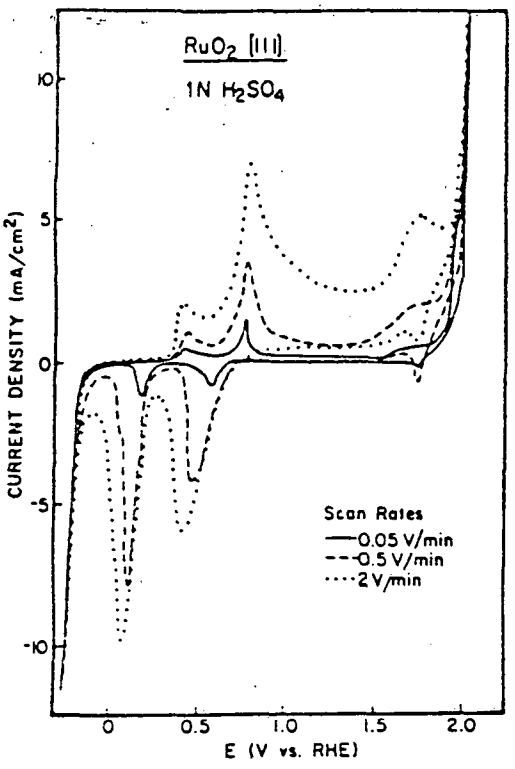

Figure 3. Cyclic voltammetry of single crystal RuO_2 with a [111] surface in a N_2 saturated solution of 1 N H_2SO_4 for several different scan rates.

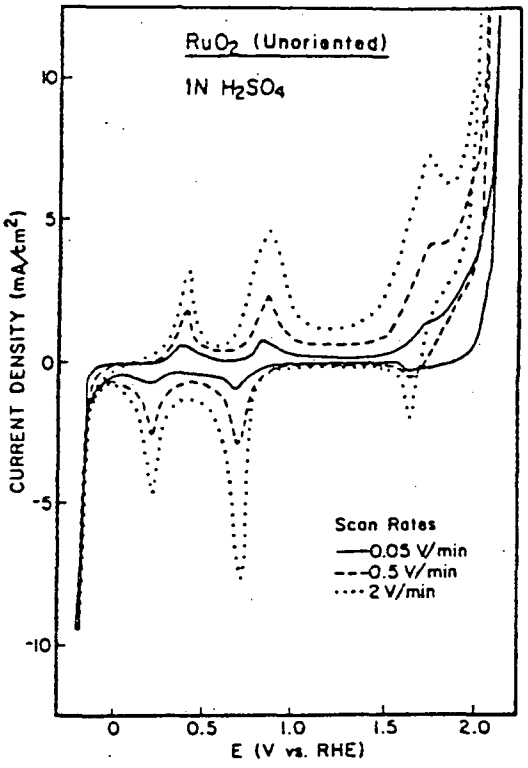

Figure 4. Cyclic voltammetry of an unoriented single crystal of RuO_2 in a N_2 saturated solution of 1 N H_2SO_4 for several different scan rates.

for the cathodic features (averaging out the structure in each case). For the unoriented sample (Figure 4) no structure is seen on either the anodic or cathodic peaks. In addition, the voltage difference between corresponding anodic and cathodic peaks is less than for the oriented samples. We attribute the observed structure in the cyclic voltammograms below 1.5 V vs RHE to the Ru_2O_3/Ru (lowest voltage anodic-cathodic pair) and the Ru_2O_3/RuO_2 couple.

Recently several investigators[8,9] have studied the electrochemical properties of RuO_2 including some work on oriented single crystals by Shafer et al.[13] They also report structure in the same general voltage range where we have seen features (although there are some differences in values) and also attribute them to the above mentioned couples. However, our cyclic voltammetry peaks are much sharper and reveal more structure than those observed by other workers.

Shafer et al report that no obvious differences were seen between the six different crystal faces that they studied.[13] Also their cyclic voltammetry curves taken on individual faces were similar to those on thermally oxidized Ru-metal. In contrast we have seen some interesting differences for the different crystallographic orientations (Figs. 1, 2 and 3).

At voltages above 1.5 V vs RHE there are also some interesting relations between the four situations we have studied. For all cases, including the unoriented sample, there is a well-defined anodic structure (~1.7 V vs RHE) preceeding the onset of the OER. There is a corresponding cathodic peak for the [110], [111] and unoriented cases but none is observed for the [100] face. These anodic features occur at the same voltage for the four samples but for the cathodic peak there is a small difference for the unoriented sample.

A similar anodic process has been observed in the case of single crystal IrO_2 (labelled A in Figure 2 of Ref. 10) and has been associated with the oxidation of IrO_2 to the higher state IrO_3. Therefore, we attribute the feature at about 1.7 V vs RHE in our case to the oxidation of RuO_2 to RuO_3.

In terms of the OER potential the [111] face shows no dependence on sweep rate (see Fig. 3) while for the other cases there are shifts to higher voltages with decreasing scan speed. We have also investigated cyclic voltammetry for Ru metal in a 1 N H_2SO_4 solution saturated with N_2 for the same scan speeds used in the RuO_2 cases. In the case of the Ru metal the OER potential does not depend on scan rate, similar to our observations for the [111] face. Although we do not completely understand these differences it is interesting to

note that for the [111] orientation of rutile (the crystal structure of RuO_2) it is possible to have a crystal face free of oxygens, i.e. only metal atoms. Thus the [111] case may be closer to the metallic situation.

In addition to the cyclic voltammetry we have also studied the steady-state electrochemical behavior of the various oriented RuO_2 samples. The log current density vs potential curves, obtained by the steady state measurements in the anodic region, were linear between 1.55 and 1.8 V vs RHE. All samples showed a slight decrease in slope at about 1.8 V vs RHE. It is interesting to note that this is the voltage of the feature that we have attributed to the oxidation of RuO_2 to RuO_3. Our measured Tafel slopes were ~ 100 mV/dec with small differences between the orientations. It appears that the [100] Tafel slope is somewhat larger than those for the other two orientations although this is not conclusive. Shafer et al have also evaluated Tafel slopes for various orientations.[13] Although their general values are in agreement with ours they appear to find more of a difference for the various faces.

III. Summary of Results

We have grown large single crystals of RuO_2 by the vapor transport method. Electrochemical investigations have been carried out on various oriented surfaces of the single crystal material as well as on a sample of unoriented single crystal material. A number of significant similarities and differences have been observed between the various faces that have been studied. Our results have revealed considerably more structure in the cyclic voltammetry curves than reported by other investigators. Thus our work on oriented single crystal RuO_2 contains important information concerning the electrocatalytic process.

IV. Future Work

We plan to grow single crystals of IrO_2 in order to further develop the work reported at last year's meeting.

Additional electrochemical studies will be performed on oriented single crystals of IrO_2 and RuO_2. This includes measurements using the rotating disc electrode method to be done in collaboration with Brookhaven National Laboratory.

Preliminary optical investigations (reflectivity and photoemission) have already been performed on single crystal IrO_2. We propose a much more detailed study of this area on both IrO_2 and RuO_2 in order to gain information concerning their fundamental electronic structure.[14] The photoemission work is being done in collaboration with the University of Mons, Mons, Belgium.

Our ultimate goal is to relate the observed electrochemical behavior of single crystal IrO_2 and RuO_2 with the fundamental electronic structure.

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