

## Electrochemical hydrogen evolution on solid oxides $\text{RuO}_2$ , $\text{Ru}_{0.7}\text{Rh}_{0.3}\text{O}_2$ and $\text{IrO}_2$ from acidic water

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**Abstract.** In contrast to traditional research with pure metals and intermetallic electrocatalysts for evolving hydrogen from acidic water, solid oxide catalytic electrode materials have been investigated recently.  $\text{RuO}_2$ ,  $\text{Ru}_{0.7}\text{Rh}_{0.3}\text{O}_2$  and  $\text{IrO}_2$  pellet electrodes have been prepared and the occurrence of the hydrogen evolution reaction on these oxides has been characterised by cyclic voltammetric and galvanostatic polarization curves in 2.5 M  $\text{H}_2\text{SO}_4$  solution at room temperature. Measurements of the pH dependence of the surface charge densities on oxide particles have been carried out to correlate surface oxide properties with electrochemical properties. Reaction mechanistic pathways on metals and intermetallic compounds have incorporated the adsorption of hydrogen atoms on metal sites. It is suggested from the correlation of surface acid/base properties of oxides with their electrochemical properties that the sites of reaction are the surface oxygen atoms covalently bonded to suitable cations and possessing the appropriate energetics in the oxides.

**Keywords.** Hydrogen evolution reaction;  $\text{RuO}_2$ ,  $\text{Ru}_{0.7}\text{Rh}_{0.3}\text{O}_2$  and  $\text{IrO}_2$  electrodes; acidic water; surface Ru redox couples; acidic oxygen atoms.

### 1. Introduction

Hydrogen production by water electrolysis is a well-known process. Water electrolysis is the simplest method for producing pure hydrogen on a large scale and has naturally become an attractive technology in the hydrogen energy market. Conventionally pure metals or intermetallic compounds have been used as catalytic electrodes for evolving hydrogen from acidic water electrolyte. Accordingly, hydrogen evolution mechanistic pathways have been proposed assuming metal sites as the reaction sites. After the expansion of solid state materials research in the past two decades (Rao 1995), electrochemists have now learnt to use various solid materials for electrochemical applications. Recently, a few groups have attempted to employ metallic oxides as electrodes for evolving hydrogen from acidic electrolytes without reducing the oxides down to the metals, and at the same time preventing corrosion to the electrodes. Materials like  $\text{RuO}_2$  (Galizzioli *et al* 1975; Kotz and Stucki 1987) and  $\text{IrO}_2$  films (Boots and Trasatti 1989) and  $\text{Sr}_{1-x}\text{NbO}_{3-\delta}$  (Manoharan and Goodenough 1990) have been shown to be promising for this purpose.

In the present study, we have prepared pellet electrodes starting from  $\text{RuO}_2$ ,  $\text{Ru}_{0.7}\text{Rh}_{0.3}\text{O}_2$  and  $\text{IrO}_2$  powders and have carried out hydrogen evolution reaction (HER) electrocatalytic studies to demonstrate that oxide materials can be successfully tested as hydrogen electrode materials. pH versus surface charge density

measurements have also been carried out and correlated with electrochemical properties to deduce the reaction pathways. It is pointed out from the consideration of the acid/base properties of oxides that the reaction sites for HER are the surface oxygen atoms bonded to suitable cations.

## 2. Experimental

The commercially available  $\text{RuO}_2$  and  $\text{IrO}_2$  powders were pressed into pellets and sintered in air at  $900^\circ\text{C}$  for 24 h. The compound  $\text{Ru}_{1-x}\text{Rh}_x\text{O}_2$  ( $x = 0.3$ ) was prepared by the following procedure. Stoichiometric amounts of ruthenium and rhodium chlorides were mixed and co-precipitated by ammonia at  $\text{pH}$  9. The gels obtained were filtered, washed thoroughly with pure water and dried in an oven at  $140^\circ\text{C}$ . They were then heated in air at  $800^\circ\text{C}$  for 4 days. The black powders thus obtained were pelletized and sintered in air at  $1000^\circ\text{C}$  for 24 h. The formation of a single phase was confirmed by X-ray diffraction studies. The tetragonal lattice parameters obtained ( $a = 4.49 \text{ \AA}$  and  $c = 3.10 \text{ \AA}$ ) are in agreement with those reported in the literature (Fernandez *et al* 1983). The rhodium seems to enter the rutile structure as  $\text{Rh}^{4+}$ .

All the sintered pellets were mounted onto electrode holders and the electrochemical measurements were carried out in  $2.5 \text{ M H}_2\text{SO}_4$  solution using a conventional three-electrode cell assembly having a porous glass-separator between the working and counter electrodes as mentioned earlier (Manoharan and Goodenough 1990). All the electrode potentials are referred to the  $\text{Hg/Hg}_2\text{SO}_4$ ,  $2.5 \text{ M H}_2\text{SO}_4$  (MMS) reference electrode.

Surface charge densities of the oxide particles were determined by potentiometric acid-base titration. The oxide powders were suspended in 25 ml of an aqueous solution of  $0.004 \text{ M KOH}$  and  $0.4 \text{ M KCl}$ . The suspensions were titrated with  $0.1 \text{ M HCl}$  with continuous stirring and  $\text{N}_2$  gas bubbled through the solution to prevent contamination from the  $\text{CO}_2$  present in the air. The end-point at each point of the titration curve was determined after the  $\text{pH}$  reading became stable. Comparison of this titration curve with the one obtained with the blank solution permitted determination of the mean surface charge on the oxide particles due to protonation or deprotonation of the surface using the formula,

$$q^\pm = F VC/SW, \quad (1)$$

where  $F$  is Faraday's constant,  $V$  is the difference in the volume of the titrant with/without the powder for a given  $\text{pH}$ ,  $C$  is the concentration of the titrant,  $S$  is the BET surface area ( $\text{RuO}_2$   $7.4 \text{ m}^2/\text{g}$ ,  $\text{IrO}_2$   $8 \text{ m}^2/\text{g}$  and  $\text{Ru}_{0.7}\text{Rh}_{0.3}\text{O}_2$   $4 \text{ m}^2/\text{g}$ ), and  $W$  is the weight of powder used.

## 3. Results and discussions

Cyclic voltammogram (CV) recorded in the potential range  $-0.8$  to  $0.8 \text{ V}$  and  $-1.0$  to  $0.8 \text{ V}$  for  $\text{RuO}_2$  are shown in figure 1. As suggested by some prominent workers (Trasatti and Buzzanca 1971; Doblhofer *et al* 1978; Burke and Murphy 1979) and from the consideration of thermodynamic (Pourbiax diagram for Ru-water system), crystallographic and electronic properties, three quasi-reversible peaks seen in the CV of figure 1a can be attributed to changes in the Ru valence states (redox couple

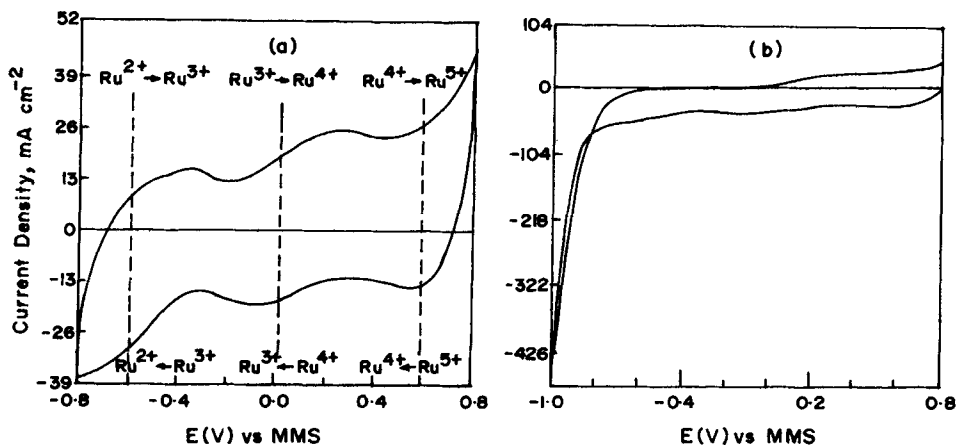


Figure 1. Cyclic voltammogram for  $\text{RuO}_2$  pellet electrode obtained in 2.5 M  $\text{H}_2\text{SO}_4$  at room temperature in the potential range  $-0.8$  to  $0.8$  V (a) and  $-1.0$  to  $0.8$  V (b). Scan rate:  $100 \text{ mVs}^{-1}$ .

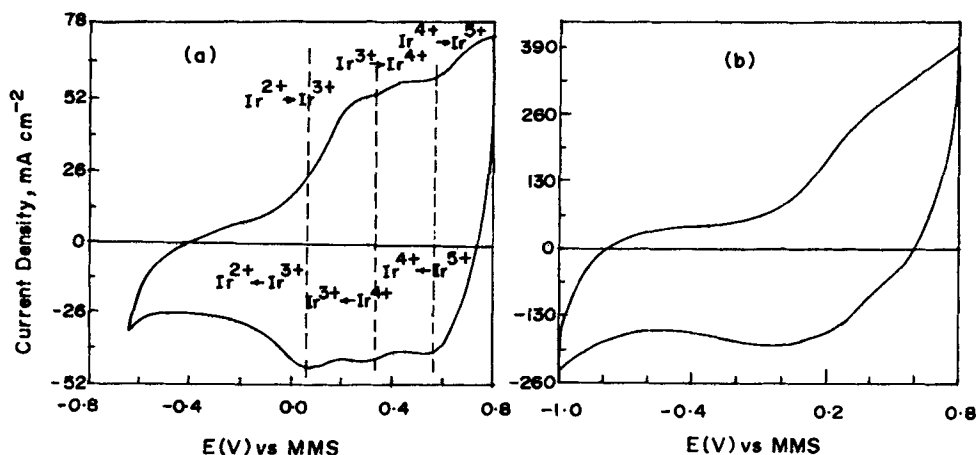


Figure 2. Cyclic voltammogram for  $\text{IrO}_2$  pellet electrode obtained in 2.5 M  $\text{H}_2\text{SO}_4$  at room temperature in the potential range  $-0.63$  to  $0.8$  V, scan rate  $10 \text{ mVs}^{-1}$  (a) and  $-1.0$  to  $0.8$  V, scan rate  $100 \text{ mVs}^{-1}$  (b).

$\text{Ru}^{2+/3+}$  at about  $-0.6$  V,  $\text{Ru}^{3+/4+}$  couple at about  $0.02$  V and  $\text{Ru}^{4+/5+}$  at about  $0.6$  V) taking place on the surface of the ruthenium dioxide during the potential scanning. When the potential is swept into the cathodic direction, as in figure 1b, heavy hydrogen evolution takes place after the  $\text{Ru}^{2+/3+}$  couple has been formed on the surface. Reduction of metal oxide down to metal does not take place.

Variation of valence states of surface metal ions and evolution of hydrogen gas have been noticed for the materials  $\text{IrO}_2$  and  $\text{Ru}_{0.7}\text{Rh}_{0.3}\text{O}_2$  also and their CVs are shown in figures 2 and 3. The CV of figure 2a has been recorded at a scan rate of  $10 \text{ mVs}^{-1}$  and that of figure 2b at a scan rate of  $100 \text{ mVs}^{-1}$ . In contrast to other materials, the sample of  $\text{IrO}_2$  in this study does not clearly show up the features corresponding to changes in Ir value states when the CV is recorded at a scan rate

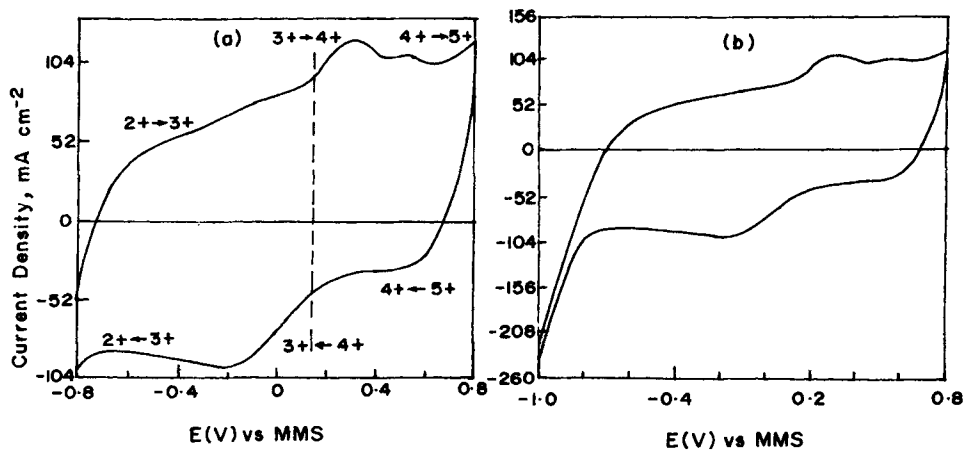


Figure 3. Cyclic voltammogram for  $\text{Ru}_{0.7}\text{Rh}_{0.3}\text{O}_2$  pellet electrode obtained in 2.5 M  $\text{H}_2\text{SO}_4$  at room temperature in the potential range  $-0.8$  to  $0.8$  V (a) and  $-1.0$  to  $0.8$  V (b). Scan rate:  $100 \text{ mVs}^{-1}$ .

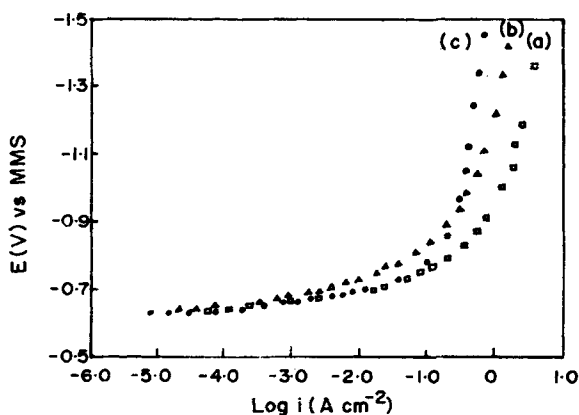


Figure 4. Tafel curves for  $\text{H}_2$  evolution on (a)  $\text{RuO}_2$ , (b)  $\text{IrO}_2$  and (c)  $\text{Ru}_{0.7}\text{Rh}_{0.3}\text{O}_2$ .

of  $100 \text{ mVs}^{-1}$ . Only at slower scan rates such as  $10 \text{ mVs}^{-1}$  are the distinguishing features clearly seen. We have recorded the CV of figure 2b at  $100 \text{ mVs}^{-1}$  to maintain consistency with the other CVs of the text. In figure 3, introduction of Rh into  $\text{RuO}_2$  has changed the features of the  $\text{RuO}_2$  CV drastically. Prominent peaks appearing at around  $0.15$  V may be attributed to the occurrence of the  $3+/4+$  couple of Rh along with that of Ru and peaks appearing at  $E < -0.4$  V and at  $E > 0.4$  V to the occurrence of  $2+/3+$  and  $4+/5+$  couples respectively.

Galvanostatic polarization curves obtained for the HER on the oxide electrode at  $25^\circ\text{C}$  are shown in figure 4. The sintered electrodes of  $\text{RuO}_2$  and  $\text{Ru}_{0.7}\text{Rh}_{0.3}\text{O}_2$  have a Tafel slope of  $30 \text{ mV/dec}$  and the sintered  $\text{IrO}_2$  electrode has a Tafel slope of  $40 \text{ mV/dec}$ . The reversible hydrogen potential (i.e.  $-0.63$  V vs MMS or  $0$  V vs NHE) has been noticed under open circuit voltage conditions on these electrodes after a

strong hydrogen discharge in  $H_2$  saturated solutions. All these data indicate that the present oxide materials are suitable for use as hydrogen evolving electrodes.

At the surface of an oxide particle in aqueous solutions the surface cations bind water in order to complete their oxygen co-ordination (England *et al* 1980). In the case of oxide powders which have fixed particle size distribution and crystallinity, the protons of the water molecules redistribute themselves over the surface and also attain equilibrium with the  $pH$  of the solution. If the protons are lost to the solution, the oxide particles become negatively charged; if protons are added from the solution to the surface, the particles become positively charged. The point of zero zeta potential (pzpz) is the  $pH$  of zero net surface charge. The addition of protons to the surface or the loosing of protons from the surface to the solution is governed by the strength of the oxygen bonding to the cation of the oxide. When this binding is covalently strong, bonding to the protons is weak and the oxide is "acidic"—protons will be released into the solution. When metal–oxygen bonding is covalently weak, the bonding of the protons is strong and the oxide is "basic"—protons will be added to the surface from the solution. Two consequences follow from this binding of surface water: (i) Chemical reactions at oxide surface involve the surface oxygen species; access to a surface cation is only via a displacement reaction: (ii) Exchange of protons between the surface oxygen atoms of a particle and aqueous oxygen allow the total surface charge on the particle to remain in equilibrium with the  $pH$  of the solution. Therefore, in our reaction equations we have to restrict ourselves to the retention of the surface charge on the particle as in any surface reaction pathway at a constant solution  $pH$  (Goodenough *et al* 1990).

$RuO_2$ ,  $Ru_{0.7}Rh_{0.3}O_2$  and  $IrO_2$  have the rutile surface structure. The  $pH$  dependence of the mean surface-charge densities of these oxides is shown in figure 5. The surface-charge densities are near zero in the range  $4 < pH < 7$  for  $RuO_2$  and  $IrO_2$  and in the range  $4 < pH < 7.93$  for  $Ru_{0.7}Rh_{0.3}O_2$ . At higher  $pH$  solutions, the oxide particles are negatively charged and at  $pH < 4$ , they are positively charged. These suggest that rutile oxides have a set of distinguishable sites that are nearly all vacant in the dry state. It is more difficult to identify these sites with certainty since the bulk oxygens are all energetically equivalent. However, two types of surface oxygen atoms are present: bridging and terminal oxygen atoms. The bridging oxygen would

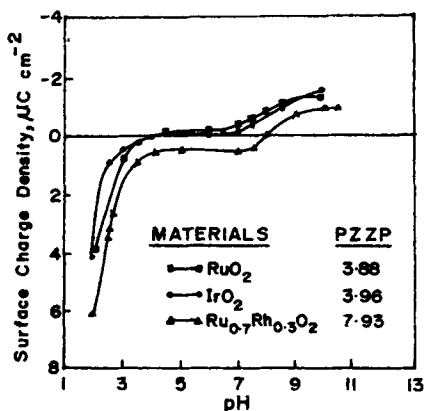
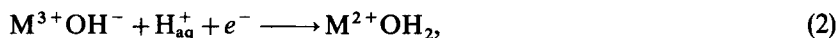


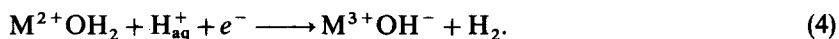
Figure 5. Surface charge densities of the oxide particles immersed in aqueous solutions of constant ionic strength.

be more tightly bound and hence more acidic; therefore it can be assumed that on these oxides, terminal oxygens are mostly missing in the dry state. In solution, these sites are occupied by the oxygen of water molecules; and in the pH region where the oxides exhibit neutral charge densities, the oxygen atoms remain as H<sub>2</sub>O. Protonation of the bridging oxygen atoms sets in at pH < 4. Once they are protonated they can evolve hydrogen very well in acid and it is possible to obtain the reversible potential of hydrogen if the solution is saturated with hydrogen. It is to be noted that the magnitude of surface charge densities will change if the number of sites accessible to hydrated protons is changed. Nature of protonation will change if there is a structural change in metal–oxygen bonding.

During the cathodic HER process we may envisage the following reactions:



and/or



[Here M represents Ru for RuO<sub>2</sub>, Ru and/or Rh for Ru<sub>0.7</sub>Rh<sub>0.3</sub>O<sub>2</sub> and Ir for IrO<sub>2</sub>] since the surface M<sup>3+/2+</sup> couple precedes the HER on the cathodic sweep. Observations of *b* = 30 mV/dec for RuO<sub>2</sub> and Ru<sub>0.7</sub>Rh<sub>0.3</sub>O<sub>2</sub> in the Tafel polarization curves suggest that reaction (2) is the rate-determining step for these oxides. Reaction (3) is the rate-determining step for IrO<sub>2</sub>, as *b* = 40 mV/dec.

Determination of the fact that the surface oxygen atoms bonded to suitable cations possessing suitable energy levels are the reaction sites for the HER is of great significance. This opens the possibility for designing various oxide materials systematically for various reactions in the fields of catalysis and electrocatalysis.

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