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SOME EFFECTS OF ELECTRONIC STRUCTURE ON THE REDUCTION OF OXYGEN ON Pt-Rh ALLOY ELECTRODES

By

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Abstract

The rest potential was determined for a series of Pt-Rh alloy electrodes in O_2-saturated, 2N H_2SO_4 solution as a function of the partial pressure of O_2 and the composition of the electrode material. In addition, the coverage of these electrodes with adsorbed oxygen was measured as a function of the composition of the electrode material by means of a cathodic stripping technique. The oxygen coverage was increased, and the rest potential was shifted to less noble values as the Rh content of the Pt-Rh alloy was increased. A suggesed explanation is as follows. As the Rh content of the electrode material is increased, the number of holes in the d-band of the alloy is increased and more bonds can be made with oxygen atoms, thus increasing the surface coverage. With increasing oxygen coverage the rate of reduction of O_2 is decreased, and the rest potential is shifted to less noble values.

Introduction

In many electrochemical processes, the electrode reaction proceeds through a step which involves the adsorption of an atom, molecule, or radical. From a theoretial standpoint, RÜETSCHI and DELAHAY[1] have shown that the hydrogen overvoltage on a number of metals is a linear function of the heat of adsorption of hydrogen; and both PARSONS[2] and GERISCHER[3] have derived expressions for the relationship between exchange current density, i_0, and the heat of adsorption of hydrogen for the various mechanisms for the cathodic evolution of hydrogen. It has been possible to correlate the heat of adsorption of hydrogen with the number of holes in the d-band[4~6] in experiments designed in such a way that the electronic structure of a transition metal was continuously modified by alloying it with another suitable metal. The dependence of the rate of the cathodic evolution of hydrogen on the electronic structure of a number of alloy electrode systems has been demonstrated[7~9] in

the literature. Recently the rate of oxidation of H_2 on Teflon-bonded Au-Pd diffusion electrodes was found[10] to vary with the composition of the Au-Pd alloy powder.

RÜETSCHI and DELAHAY[1] have also shown from theoretical considerations that variations in the oxygen overvoltage from one metal to the other may be correlated with the energy of the M–OH bond. It is possible that the electronic structure would influence the electrochemical properties of the oxygen electrode. However, MACDONALD and CONWAY[12] could not find any d-band effects of the electronic structure of a series of Au–Pd anodes on evolution of oxygen from both acid and alkaline solutions. Most likely, the formation of anodic oxide films on the anode surface obscured such effects since the evolution of oxygen takes place on the surface of the oxide film.[13] The anodic evolution[14,15] and cathodic reduction[15,16] of O_2 on noble metal alloy electrodes have been carried out; but even though the alloys seemed to have a lower value of the overvoltage, effects of the electronic structure were not evident,

If the interaction of O_2 with the electrode surface could be studied on a series of alloys before the interfering adsorbed oxide film is formed, the dependence on the electronic structure might be observed. RAO and co-workers[17] investigated the adsorption of O_2 on oxide-free surfaces of Pt, Pd, Rh, Ir and, Au wires from O_2-saturated, H_2SO_4 solutions. The oxygen adsorbed over a period of about 30 min was determined by constant current stripping experiments. For those metals having 0.6 hole in the d-band (Pt and Pd), the surface was about 25% covered; for those having nearly 2 holes (Rh, Ir), about 100%; for those with zero hole (Au), about 3%.

It is the purpose of this report to describe a series of experiments carried out on a series of Pt–Rh alloys and designed to demonstrate the influence of the electronic structure of the electrode material on the electrochemical parameters of the O_2 electrode at rest. Platinum and rhodium were chosen because these metals form completely miscible solid solutions over the entire composition range and the composition of the liquidus phase is nearly the same as the solidus.[18] As a result, thermal treatment of these alloys is unlikely to produce significant changes in the physical properties. Both Pt and Rh form highly unstable oxides,[12,19,20] and both can dissolve oxygen in the surface layers of the metal (dermasorbed[21] oxygen). As Rh is added to Pt, it is assumed that the number of holes in the alloy d-band increases continuously.

Experimental

Rigorous control of impurities was maintained throughout the investigation,

and a Teflon cell was used.[22] The alloys in the form of wires (99.9+% pure) were obtained from Englehard Industries, Inc., and had the following compositions: 9.2, 17.4, 38.8, 65.5, 85.1, and 94.5 at. % Rh. Electrodes were formed by melting small beads (~0.15 cm in diameter) at the end of the wire in the flame of an oxygen torch. The preparation of the electrode consisted of successive rinses in benzene, acetone, and distilled water followed by a dip in concentrated HNO_3 and heating to a dull red heat in a hydrogen flame. Afterward, the lead wire was covered with tight-fitting Teflon spaghetti so that only the head of the bead was exposed; and finally, the electrode was mounted[22] in the cap of the Teflon cell. Once the cell was filled with 2N H_2SO_4 solution, the electrodes were preelectrolyzed against a removable cathode for 48 hr. Before readings were taken, the solution was saturated with H_2 followed by saturation with O_2. Steady-state rest potentials were recorded after 24 hr with O_2 flowing. The partial preassure of O_2, P_{O_2}, was varied by diluting the purified O_2 stream with purified N_2 and was monitored by a Beckman polarographic O_2 analyzer.

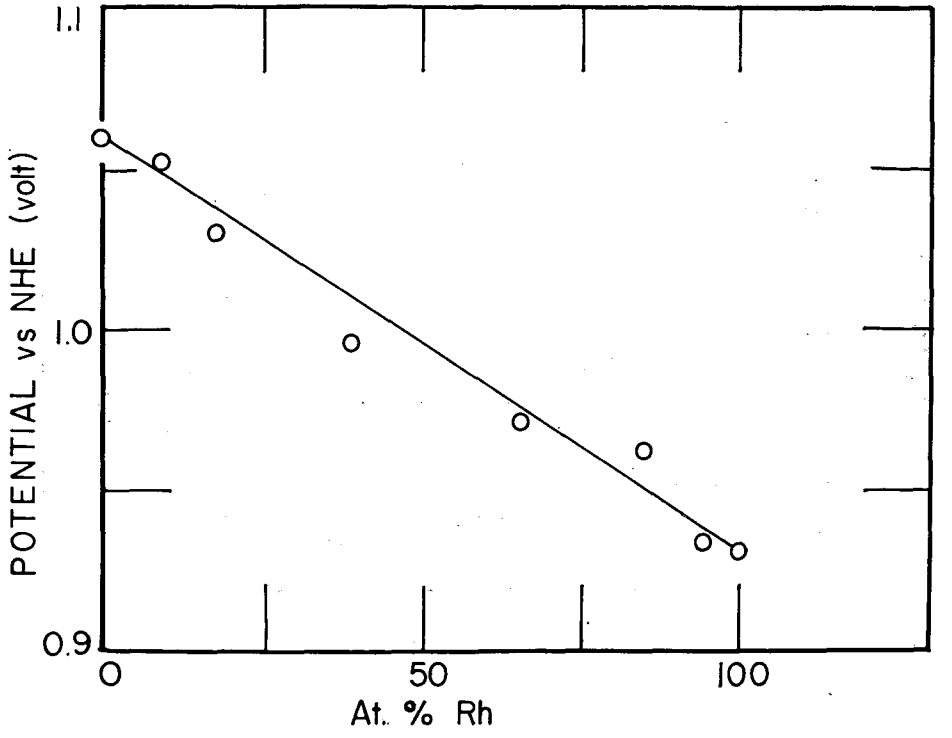

Fig. 1. The dependence of the rest potential on the composition of the alloy-oxygen-electrode material.

The coverage of the surface with adsorbed O_2, θ, was determined by applying a constant current stripping pulse to the electrode with a single-pulse circuit[23] similar to that used by HACKERMAN and co-workers.[24] A value of 1.3[25] was used as a roughness factor in area determinations, and 512 μcoul. was used as the value for complete monolayer coverage.

All potentials were measured against an α-Pd-H reference electrode[26] with

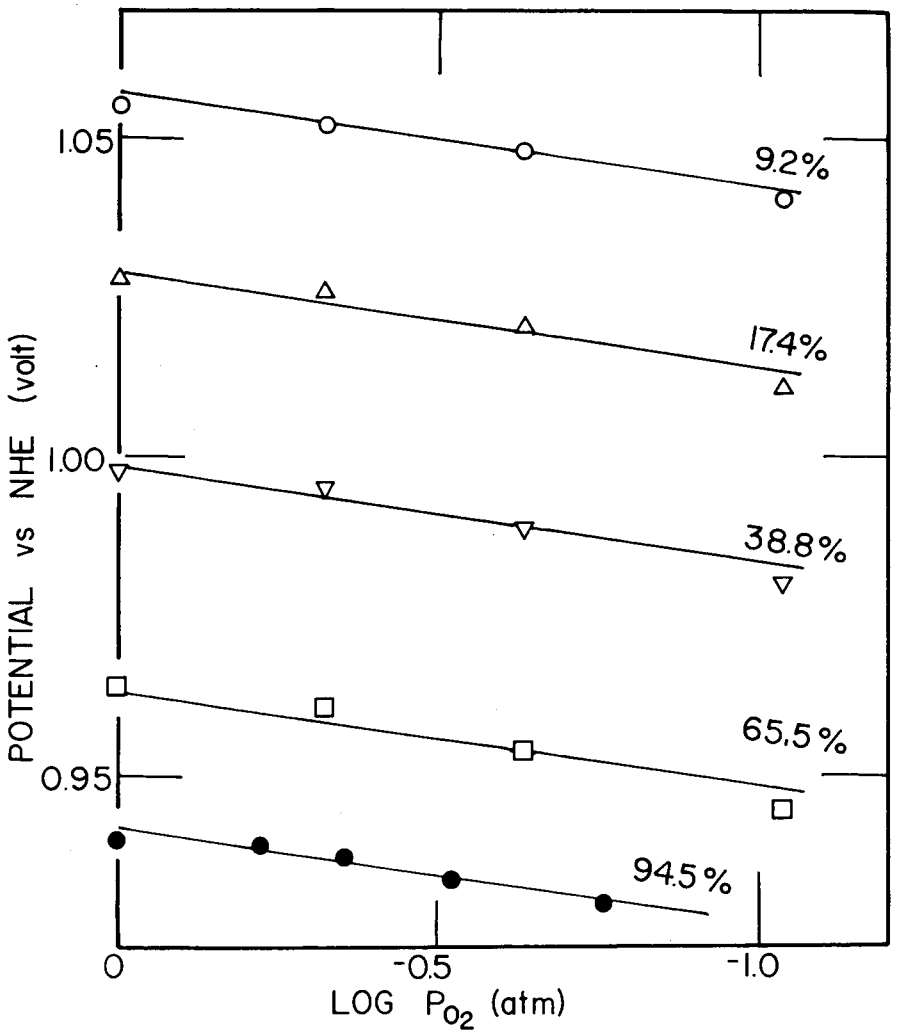

Fig. 2. The dependence of the rest potential on the log P_{O_2} for a number of Pt-Rh alloy oxygen electrodes. The atomic % Rh is noted. A 15-mV slope was drawn through the data to show that the data are consistent with a 4-electron change.

a General Radio electrometer, model 1230-A, and recorded on the normal hydrogen electrode (NHE) scale. The temperature at which this work was carried out was 24°±1°C.

Results

In Fig. 1, the steady-state rest potential of the alloy electrodes in O_2-saturated, 2 N H_2SO_4 solution is presented as a function of the alloy composition. The data of Fig. 1 are the average of three different experiments, and rest potential values for pure Pt[22] and pure Rh[20] were taken from the literature.

Typical results obtained for the variation of the rest potential with P_{O_2} are given in Fig. 2. Lines with a slope of 15 mV are drawn through the data points to show that the date are consistent with a 4-electron process.

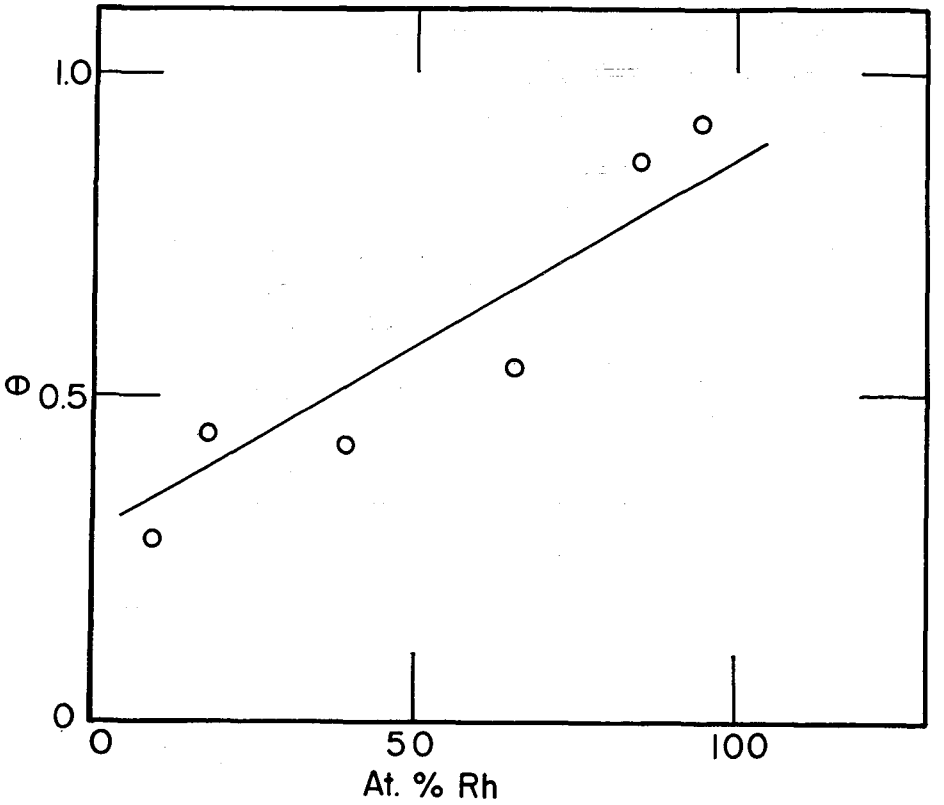

Fig. 3. Plot of the fraction of the surface covered with adsorbed oxygen as a function of the composition of the Pt-Rh alloy electrode.

The average of three separate determinations of the suface coverage, θ, on each alloy after being in contact with O_2-saturated H_2SO_4 solution for 24 hr is plotted in Fig. 3 as a function of the alloy composition. There is an estimated error of about 20% in these data; the results, however, do show a trend toward increasing coverage with increasing Rh content.

Discussion

It has been suggested[22] that the rest potential observed at a noble metal oxygen electrode may be explained in terms of a mixed potential mechanism. The partial reactions involved in determining the mixed potential are the O_2/H_2O reaction,

$$O_2 + 4H^+ + 4e \rightleftharpoons 2H_2O, \qquad (1)$$

and the Pt/Pt–O reaction[22] at a Pt electrode,

$$Pt\text{–}O + 2H^+ + 2e \rightleftharpoons H_2O, \qquad (2)$$

or the Rh/Rh–O reaction[20] at a Rh electrode,

$$Rh\text{–}O + 2H^+ + 2e \rightleftharpoons H_2O. \qquad (3)$$

The symbols Pt–O and Rh–O indicate that the surface is covered with a hydrated partial monolayer of adsorbed oxygen atoms and the local cell is set up such that the O_2/H_2O reaction is polarized cathodically while the metal-oxygen reaction (either Eq. 2 or 3) is polarized anodically as shown by curve A (Eq. 1) and curve B (Eq. 2 or Eq. 3) in Fig. 4. Where the curves cross, the potential, E^m, is the observed rest potential (mixed potential). Since $dE/d\log P_{O_2} \sim 15$ mV and since $dE/dpH \sim 60$ mV[20,22] for Pt/O_2 and Rh/O_2 electrodes, the O_2/H_2O reaction is potential-determining; and the metal-oxygen reaction is in a limiting current region at the point of the crossing of the curves.

From the data in Fig. 2, it is apparent that the O_2/H_2O reaction is the potential-determining raction at all oxygen electrodes in the series of Pt-Rh alloys. Consequently, the observed rest potentials may be described by the mechanism pictured in Fig. 4.

Cathodic stripping experiments produced results (Fig. 3) which show that the fraction of the surface covered with adsorbed oxygen atoms increases with increasing Rh content of the alloy. From triangular sweep traces,[27] rotating disc-ring studies,[28,29] and steady-state polarization measurements,[19,20] it has been shown that the presence of an adsorbed film on the electrode surface inhibits the reduction of molecular oxygen. As a result, the polari-

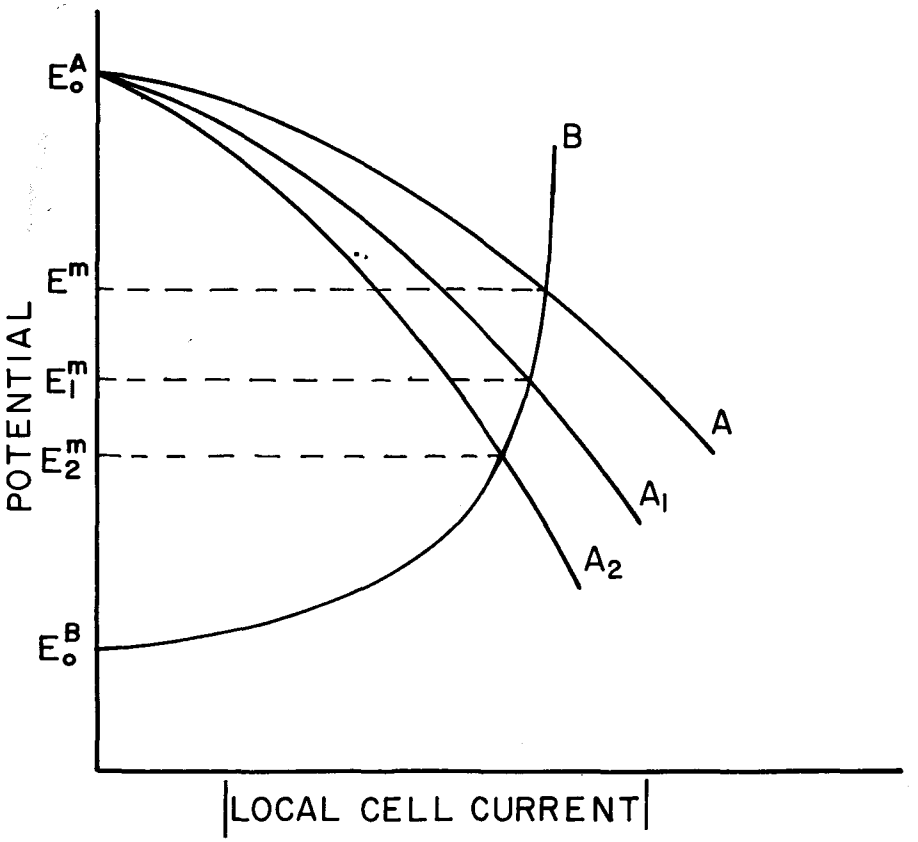

Fig. 4. A sketch of the local cell polarization curves for the O_2/H_2O reaction, curve A, and the metal/metal-oxygen reaction, curve B. Curves A_1 and A_2 represent the polarization on electrodes with increasing Rh content with corresponding mixed potentials, E_1^m, and E_2^m. E_0^A and E_0^B are the equilibrium potentials for the O_2/H_2O reaction (1,229 mV) and the metal/metal-oxygen reaction (~880 mV).

zation of the O_2/H_2O reaction for a given current density should increase as the Rh content of the electrode material is increased.

In Fig. 4, curves A_1 and A_2 represent the polarization of the O_2/H_2O reaction on Pt–Rh alloy electrodes of increasing Rh content. With the increasing surface coverage accompanying the increase in Rh content, the O_2/H_2O polarization curve is bent more strongly toward the potential axis and cuts the B curve at less noble potentials. Since the potential at the crossing of the curves is the observed rest potential, this potential is shifted to less noble values as the Rh content of the alloy increases, as demonstrated experimentally in Fig. 1.

It appears that the effect of the electronic structure of the electrode material on the rest potential depends on the amount of adsorbed oxygen atoms on the metal surface. Those alloys with a large number of holes in the d-band (high Rh content) have surfaces which can make more bonds with adsorbed oxygen atoms, and hence, have the greater surface coverage of adsorbed oxygen. When O_2 is adsorbed on Pt, it is dissociated to oxygen atoms as demonstrated by DAMJANOVIC and co-workers[17,30] who observed that a square root relationship exists between the P_{O_2} and θ. The more oxygen adsorbed on the surface, the lower is the rate of reduction of molecular oxygen on that surface. Such an effect produces a shifting of the mixed or rest potential to less noble values.

It is to be noted that the oxygen that is reduced is not dissociated until after two electrons are transferred[13] since peroxides are observed as reaction intermediates.[13, 27, 29] Possibly the adsorbed oxygen atoms occupy the available bonding sites required by molecules of oxygen for the efficient transfer of electrons in the reduction of O_2, and in this way, the adsorbed atomic oxygen film inhibits the reduction of molecular oxygen to peroxide or water. In other words, the presence of the adsorbed oxygen film makes it more difficult for the O_2 molecules to get close enough to the electrode surface to exchange an electron.

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