

Amorphous nickel-valve metal-platinum group metal alloy electrodes for hydrogen-oxygen sulphuric acid fuel cells

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Powder catalysts were prepared by immersion of amorphous Ni-40Zr and Ni-40Ti alloys containing a few at % of platinum group elements in HF solution. This treatment led to preferential dissolution of the valve metal and nickel with a consequent formation of microcrystalline alloy powders consisting of concentrated platinum group elements and some nickel and valve metal. Porous gas-diffusion electrodes prepared by using these alloy catalyst powders were employed for electrochemical reduction of oxygen and oxidation of hydrogen in 1 M H₂SO₄ at 25°C. The activity of the electrodes prepared from the amorphous alloys containing Pt-Ru, Pt-Rh, Pt and Pd for oxygen reduction was considerably higher than that of the platinum black electrode. Oxidation of hydrogen occurred readily close to the equilibrium potential. Amorphous alloy electrodes containing Pt-Ru, Pt-Rh and Pt were more active than the platinum black electrode for the hydrogen oxidation.

1. Introduction

Fuel cells are highly efficient generators. The trend is to increase the temperature of fuel cells, so as to use the electrolyte at the temperature corresponding to its highest conductivity. However, for utilization of their most attractive characteristic, that is, operation in any location, it is desirable that town gas and natural gas fuel cells can operate at ambient temperature.

Porous gas-diffusion electrodes consisting exclusively of platinum as catalyst show good performance for reduction of oxygen at elevated temperatures, e.g. in phosphoric acid fuel cells [1-8]. In order to operate fuel cells utilizing porous gas-diffusion electrodes at ambient temperature, catalysts superior to platinum are required.

Amorphous alloys have the potential for providing new catalysts or precursors of new catalysts in special reactions. Amorphous alloys form a single phase solid solution which can contain catalytically effective elements without limitation of the solid solubility in the equilibrium state. Accordingly, preparation of amorphous alloys allows modification of the electronic state of the catalyst element by alloying in addition to synergistic effects of different elements. The modification of the electronic state of catalysts and the synergistic effect of different elements offers new catalysts with high catalytic activity and selectivity for a specific reaction.

It was earlier found that, when amorphous nickel-valve metal alloys containing a few atomic percent of platinum group elements were activated by immersion in hydrofluoric acid, their surfaces became excellent electrocatalysts for chlorine production [9] and for oxidation of methanol [10]. The surface activation

treatment of these alloys is based on the selective dissolution of electro-catalytically less active valve metal and nickel with a consequent accumulation of electrocatalytically active platinum group elements in the surface layer [for example 9]. Furthermore, it was found that prolonged immersion of these amorphous alloys in hydrofluoric acid resulted in the formation of powder consisting mainly of platinum group metals and a little nickel and valve metal [10, 11]. When porous gas-diffusion electrodes were made of these powders prepared from amorphous nickel-valve metal alloys containing a few atomic percent of platinum group elements, the electrodes showed excellent performance for oxidation of methanol and reduction of oxygen in 0.5 M H₂SO₄ at ambient temperature [12].

The development of town gas fuel cells requires effective catalysts for electrochemical oxidation of town gas constituents. Since a variety of amorphous nickel-valve metal-platinum group metal alloys can be produced, some of these may be usable as catalysts. Hydrogen is a major constituent of town gas. The present work aims to examine the performance of porous gas-diffusion electrodes consisting of powder catalysts prepared from these amorphous alloys in oxidation of hydrogen and reduction of oxygen in sulphuric acid at ambient temperature.

2. Experimental details

2.1. Amorphous alloys

Crystalline nickel-valve metal-platinum group metal alloy ingots were cast by high frequency induction melting of 99.95% nickel, 99% titanium or zirconium and 99% ruthenium, rhodium, palladium, iridium

and/or platinum under an argon atmosphere. Amorphous alloys were prepared by a single roller quenching method under an argon atmosphere after re-melting these alloy ingots. The amorphous alloys were in the form of ribbons of 0.5–1 mm width and 20–40 μm thickness.

2.2. Powder catalysts and electrodes

Amorphous alloy ribbons were immersed in 46% HF solution at ambient temperature for a few tens of minutes, until hydrogen bubbling stopped. By this treatment, black catalyst powders with rough surfaces were obtained. The catalyst powders were rinsed with distilled water and then dried in a vacuum desiccator. The composition of the powder catalysts was determined by electron probe microanalysis (EPMA). The structure of the powder catalysts was examined by X-ray diffraction at θ - 2θ mode with CuK_α radiation. The catalyst powder size was estimated from the full width at half maximum of the X-ray diffraction pattern.

The catalyst powders were mixed with carbon black powder (Toka Black No. 5500), polytetrafluoroethylene (PTFE) dispersion and sucrose in an agate mortar with an agate pestle. The weight ratio of catalyst powder, carbon black powder, PTFE dispersion and sucrose was 7:3:3:10. The paste thus prepared was coated onto a carbon paper which had been previously immersed in PTFE, followed by heating at 100°C for 5 min in order to provide the hydrophobicity to the gas supplying side of the electrode. After drying in air for more than 1 day, the catalyst-coated carbon paper was baked at 370°C for about 20 min in a stream of nitrogen. By this procedure porous gas-diffusion electrodes were obtained, the reaction side of which was composed of the catalysts prepared from the amorphous nickel-valve metal alloys containing a few atomic percent of platinum group elements. The electrode thus prepared is termed the amorphous alloy electrode. The platinum black electrode using platinum black powder catalyst was also prepared using a similar procedure including mixing the platinum black powder with carbon powder, PTFE and sucrose.

2.3. Electrochemical measurements

The reaction side of the electrode, 10 mm in diameter, was exposed to the electrolyte. The electrolyte was 1 M H_2SO_4 maintained at $25 \pm 0.1^\circ\text{C}$ by water circulation through the jackets of the two compartments of the cell. The solution was deaerated by bubbling a stream of oxygen-free nitrogen for more than 20 h. A platinum gauze and a saturated calomel electrode were used as counter and reference electrodes, respectively.

Cyclic voltammetry was performed between -8 mV (NHE) and 1592 mV (NHE) with a sweep rate of 50 mV s^{-1} for activation of the electrode for more than 20 min with oxygen-free nitrogen passing through the gas compartment.

The electrode performance for oxygen reduction and hydrogen oxidation was potentiodynamically examined with a potential sweep rate of 50 mV min^{-1} by passing air and hydrogen streams through the gas compartment, respectively. Correction for ohmic drop was made using a Hokuto IR Compensation Instrument, when necessary.

3. Results and discussion

3.1. Characterization of powder catalysts

X-ray diffraction patterns of catalyst powders formed by HF treatment of the amorphous alloys containing platinum revealed that the powders were composed of fcc microcrystallites whose lattice constants were all a little smaller than the lattice constant of platinum. This indicates that the microcrystallites are not platinum metal but platinum-base alloys. It is known [9] that immersion of these amorphous alloys in HF solution results in preferential dissolution of the valve metal and nickel. Accordingly, the X-ray diffraction patterns suggest that the microcrystallites consist of the fcc solid solution of Pt with some Ni and Zr or Ti. The catalyst powders prepared from the other alloys, except for the ruthenium-containing alloys, exhibited similar fcc patterns corresponding to the platinum group elements contained in the amorphous alloys, although the lattice constants were always smaller than those of the single platinum group metals. When the amorphous alloys contained ruthenium, the catalyst powder formed by HF treatment did not show a diffraction pattern corresponding to the hcp ruthenium phase, but gave a halo pattern similar to that for the amorphous alloy ribbon, although the first halo shifted to 0.205 nm which was close to 101 reflection of the hcp Ru.

Table 1 shows the composition of the catalyst powder determined by EPMA. This shows that the HF treatment results in a remarkable accumulation of platinum group elements. According to analyses of some powders by analytical electron microscopy (AEM) and X-ray photoelectron spectroscopy (XPS) [11], the analytical results by EPMA almost coincided with those obtained by AEM and XPS. Consequently, the composition of the catalyst powders is similar for their surfaces and bulk. Almost all the platinum group elements remained in the catalyst powders without dissolution during the HF treatment. The content of the platinum group elements in the catalyst powders increases slightly with increasing concentration of platinum group element in the amorphous alloys. In spite of the fact that the platinum group elements were a few atomic percent, they accumulated to more than 50 at %. Accordingly, almost the entire alloy was dissolved into the HF solution, and the platinum group metal-base solid solutions were constructed by the platinum group elements, some nickel and very small amounts of zirconium or titanium which remained without dissolution.

It is noteworthy that, when two kinds of platinum

Table 1. Compositions of catalyst powders prepared from amorphous alloys (at %)

Amorphous alloys (at %)	Ni	Zr	Ti	Ru	Rh	Pd	Ir	Pt
Ni-40Zr-1Ru	42.93	2.39		54.68				
Ni-40Zr-3Ru	44.41	4.36		51.23				
Ni-40Zr-5Ru	28.22	3.86		67.92				
Ni-40Zr-1Rh	25.63	4.45			69.92			
Ni-40Zr-3Rh	20.27	3.44			76.29			
Ni-40Zr-5Rh	19.22	4.07			76.71			
Ni-40Zr-1Pd	19.56	2.17				78.27		
Ni-40Zr-3Pd	14.67	2.43				82.90		
Ni-40Zr-5Pd	12.82	2.93				84.25		
Ni-40Zr-1Ir	33.84	5.38					60.78	
Ni-40Zr-3Ir	28.05	4.81					67.14	
Ni-40Zr-5Ir	29.20	7.90					62.90	
Ni-40Zr-1Pt	31.29	5.58						63.13
Ni-40Zr-3Pt	37.04	3.54						59.42
Ni-40Zr-5Pt	21.40	5.38						73.22
Ni-40Ti-3Ru	32.00		8.89	59.11				
Ni-40Ti-3Rh	23.42		2.44		74.14			
Ni-40Ti-3Pd	14.73		5.40			79.87		
Ni-40Ti-3Pt	24.77		2.14					73.09
Ni-40Zr-1.5Ru-1.5Rh	30.34	3.61		33.43	32.62			
Ni-40Zr-1.5Ru-1.5Pd	22.80	3.96		37.64		35.60		
Ni-40Zr-2.0Ru-1.0Pt	32.46	7.09		40.52				19.93
Ni-40Zr-1.5Ru-1.5Pt	17.91	5.25		38.52				38.32
Ni-40Zr-1.5Rh-1.5Pt	27.23	7.50			31.23			34.04

group elements are contained in the alloys, the ratio of the two elements in the catalyst powder is almost the same as that in the amorphous alloy in spite of the fact that most of the nickel and zirconium was dissolved in the HF solution.

Table 2 shows the sizes of catalyst powders estimated from full widths at half maxima of 111 and 222 reflections of the fcc phase in their X-ray diffraction patterns. The catalyst powders consist of very fine grains of about 2–3 nm, almost regardless of platinum group elements and of their content in the amorphous alloys.

Consequently, the very fine catalyst powders prepared from the amorphous alloys are not composed of single platinum group metals but of their

alloys. The alloy catalysts may have the synergistic effect of alloy constituents in catalysis in addition to the modification of the electronic state of the catalytically active element by alloying. It may, therefore, be expected that high catalytic activity occurs due to the very fine alloy particles.

3.2. Electrode performance

3.2.1. Cyclic voltammetry. Preliminary knowledge of the stability and activity of the electrode was obtained by cyclic voltammetry with passage of nitrogen in the gas compartment, although previous cyclic voltammetry was necessary in activating the catalysts covered by air oxidation products.

Figure 1 shows the cyclic voltammogram of the electrode prepared from the amorphous Ni-40Zr-1Ru alloy. The repetitive cyclic voltammetry leads to a monotonic increase in the current at almost all potentials. Ruthenium has the lowest corrosion resistance among platinum group metals [13], and nickel-valve metal-ruthenium alloys are also less corrosion-resistant in sulphuric acid [14]. The increase in the current with repeated cycling is not attributable to an increase in the wettability of the electrode but to an increase in amounts of oxide formation and its reduction. Accordingly, the electrodes prepared from the amorphous nickel-valve metal-ruthenium alloys cannot be expected to have a high corrosion resistance in the sulphuric acid.

Figure 2 shows the cyclic voltammogram of the electrode prepared from the amorphous Ni-40Zr-3Pd alloy. Two anodic peaks at potentials higher than

Table 2. Sizes of catalyst powders prepared from amorphous alloys (at %)

Amorphous alloys (at %)	Powder diameter (nm)
Ni-40Zr-1Rh	2.38
Ni-40Zr-3Rh	2.52
Ni-40Zr-5Rh	2.20
Ni-40Zr-1Pd	2.87
Ni-40Zr-3Pd	3.60
Ni-40Zr-5Pd	3.07
Ni-40Zr-3Ir	2.29
Ni-40Zr-5Ir	2.05
Ni-40Zr-3Pt	2.56
Ni-40Ti-3Rh	2.33
Ni-40Ti-3Pd	2.55
Ni-40Ti-3Pt	2.84
Platinum black	7.25

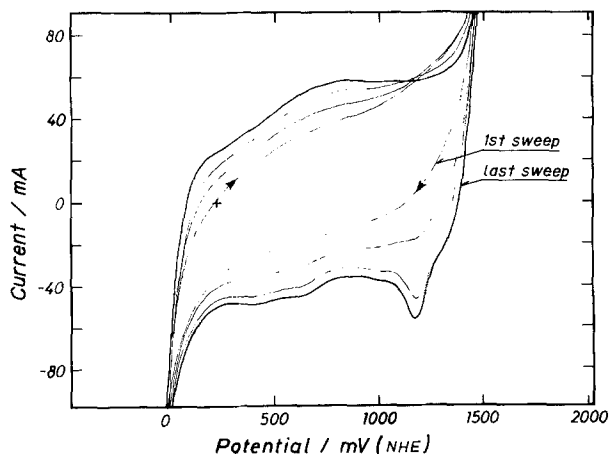


Fig. 1. Cyclic voltammogram of the electrode prepared from the amorphous Ni-40Zr-1Ru alloy measured in 1 M H_2SO_4 at 25°C with passage of nitrogen in the gas compartment.

750 mV (NHE) are attributable to adsorption of oxygen species. The cathodic peak at about 610 mV (NHE) arises from reduction of the adsorbed oxygen species. Since the latter peak appears at a relatively high potential, the electrode containing palladium may have a high activity for oxygen reduction. A similar voltammogram was obtained for the electrode prepared from platinum-containing alloys. Adsorption of oxygen and its reduction on the electrode prepared from rhodium-containing alloys did not occur readily, but oxidation of adsorbed hydrogen took place easily on the electrode. Accordingly, this electrode may be suitable as a hydrogen fuel electrode. As shown in Fig. 3, the electrode containing iridium exhibited large currents for oxidation and reduction at potentials higher than 800 mV (NHE), where formation and reduction of Ir_2O_3 and IrO_2 occurs. This suggests that the iridium-containing electrode may not be suitable for both hydrogen oxidation and oxygen reduction.

3.2.2. Reduction of oxygen. Figure 4 shows potentiodynamic polarization curves of electrodes prepared from the platinum-containing alloys for oxygen reduction. The effective surface areas of the electrodes

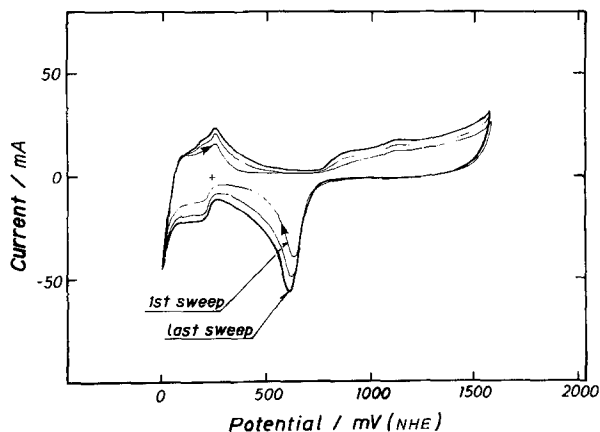


Fig. 2. Cyclic voltammogram of the electrode prepared from the amorphous Ni-40Zr-3Pd alloy measured in 1 M H_2SO_4 with passage of nitrogen in the gas compartment.

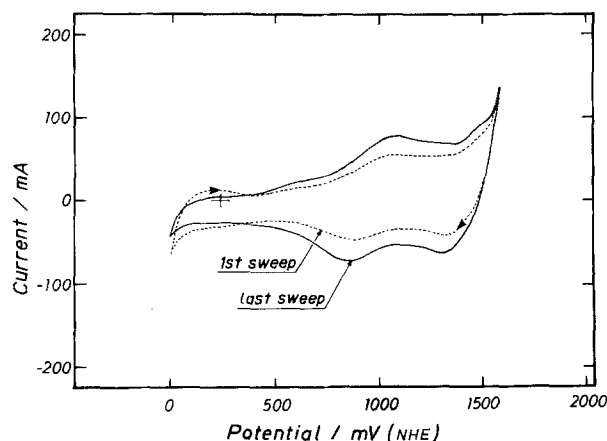


Fig. 3. Cyclic voltammogram of the electrode prepared from the amorphous Ni-40Zr-3Ir alloy measured in 1 M H_2SO_4 at 25°C with passage of nitrogen in the gas compartment.

and the weights of platinum group elements were different from one electrode to another, although the weight of catalyst powder was fixed for all the electrodes. Hence, the current was expressed in amperes per mole of the platinum group element in the electrode, which was estimated from the weight of the catalyst and the concentration of the platinum group element given in Table 1. The overvoltages of the platinum-containing electrodes for oxygen reduction are about 250–270 mV, which are the lowest among the electrodes containing various single platinum group elements.

Figure 5 shows potentiodynamic polarization curves for electrodes containing different platinum group elements. The polarization curve in the figure was that measured for the electrode having the highest activity among the electrodes containing the same kind of platinum group element. The polarization curve for the platinum black electrode is also included for comparison. The amorphous alloy electrodes, except for the electrode containing ruthenium, have higher activities for oxygen reduction than that of the platinum black electrode. In particular, the electrodes

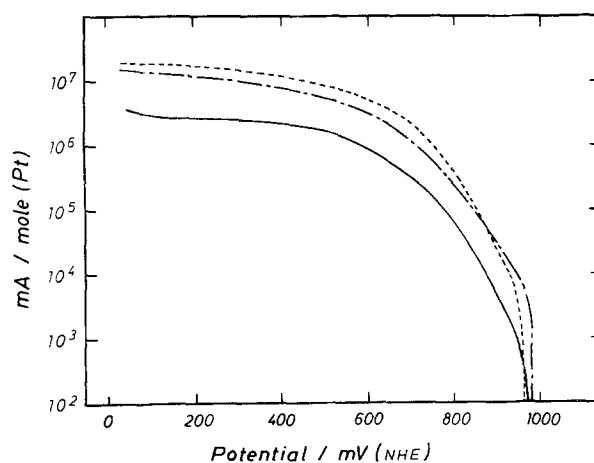


Fig. 4. Potentiodynamic polarization curves of the electrodes prepared from the amorphous Ni-40Zr- x Pt alloys containing 1–3 at % of platinum for oxygen reduction measured in 1 M H_2SO_4 at 25°C with passage of air in the gas compartment. (---) $x = 1$, (- - -) $x = 3$, (—) $x = 5$.

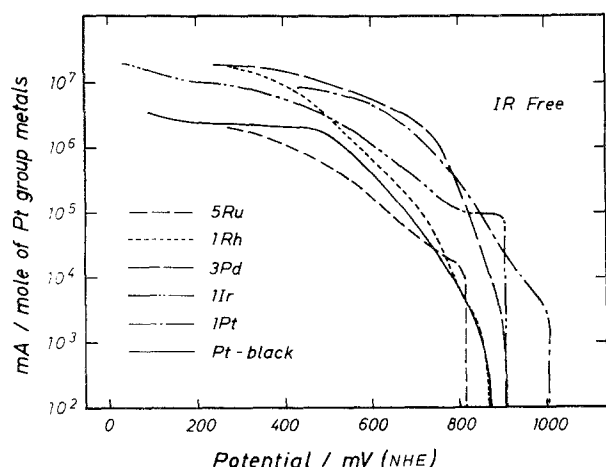


Fig. 5. Potentiodynamic polarization curves of the electrodes prepared from the amorphous Ni-40Zr alloys containing different platinum group elements (xM) for oxygen reduction measured in 1 M H_2SO_4 at 25°C with passage of air in the gas compartment. Corrections for ohmic drop were made.

containing palladium or platinum have very high activities. The increasing order of the oxygen reduction activity of the amorphous alloy electrodes is almost the same as the decreasing order of the oxygen reduction overvoltage of the single platinum group elements contained in the amorphous alloy electrodes, that is, ruthenium > rhodium > iridium > palladium > platinum. The sharp current increase for ruthenium- and iridium-containing alloy electrodes close to open circuit potentials is probably due to reduction of oxides formed during the previous cyclic voltammetry.

The apparent Tafel slopes observed from the linear portions of the polarization curves can be classified into three groups. The Tafel slope for the ruthenium- and iridium-containing electrodes is about $-180 \text{ mV decade}^{-1}$, that for the platinum- and rhodium-containing electrodes is about $-120 \text{ mV decade}^{-1}$ and that for the palladium-containing electrode is about $-60 \text{ mV decade}^{-1}$. Although the Tafel slope for the palladium-containing electrode is smaller than that for the platinum-containing amorphous alloy elec-

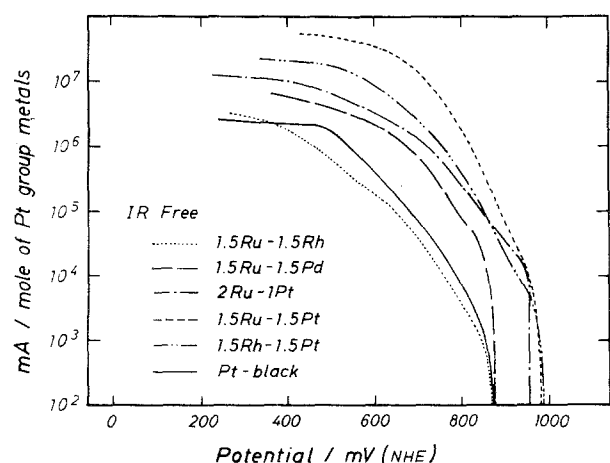


Fig. 6. Potentiodynamic polarization curves of the electrodes prepared from the amorphous Ni-40Zr alloys containing different sets of two kinds of platinum group elements ($xM_1 - yM_2$) for oxygen reduction measured in 1 M H_2SO_4 with passage of air in the gas compartment. Corrections for ohmic drop were made.

trode, the absolute current for the former electrode is not higher than that for the latter electrode at high potentials because of the higher overvoltage of the former electrode for oxygen reduction.

The change in the Tafel slope for oxygen reduction, depending upon the reaction mechanism, has been discussed in detail by Damjanovic *et al.* [15]. The Tafel slope for oxygen reduction on platinum metal in 1 M H_2SO_4 at 50°C and 70°C is reported as $-65 \pm 5 \text{ mV decade}^{-1}$ at potentials higher than 800 mV (NHE) [16], and that on a Teflon-backed platinum black electrode in 85% H_3PO_4 at 120°C is about -60 and $-120 \text{ mV decade}^{-1}$ at low and high current densities, respectively [2]. The Tafel slope for the oxygen reduction on the oxide covered rhodium metal in 1 M H_2SO_4 at 25°C has been known to be about $-120 \text{ mV decade}^{-1}$ [for example 17], and that on the reduced rhodium metal is close to -60 and $-120 \text{ mV decade}^{-1}$ at low and high current densities, respectively, at 25°C [18].

The Tafel slope of the platinum- and rhodium-containing amorphous alloy electrodes seems to coincide with these previously reported values for the platinum group metals, although it is difficult to estimate the effect of temperature on the data for the platinum electrodes measured at 120°C. In the present experiment, the reaction order of oxygen was not determined, but the mechanism for oxygen reduction may be different among the above mentioned three groups of electrodes.

The change of valve metal from zirconium to titanium in the amorphous alloys led to no change in the polarization curves, and had no effect on the activity of the electrodes for oxygen reduction.

Combined additions of two kinds of platinum group elements sometimes gave rise to a significant increase in the activity for oxygen reduction. Examples are shown in Fig. 6. The low overvoltage for oxygen reduction is effected by the platinum-containing electrodes. The overvoltage of the platinum-containing electrodes is about 250 mV, while that of the electrodes without platinum is higher than about 350 mV. The combined addition of platinum and ruthenium or platinum and rhodium decreases the Tafel slope. Consequently, the electrodes prepared from the amorphous Ni-40Zr-1.5Ru-1.5Pt and Ni-40Zr-1.5Rh-1.5Pt alloys have very high activities, which are higher than those of the electrodes prepared from the amorphous Ni-40Zr-Pt alloys. However, the electrode prepared from the amorphous Ni-40Zr-2Ru-1Pt alloy has almost the same Tafel slope as that for the electrode prepared from the Ni-40Zr-1Pt alloy, and hence their polarization curves are almost the same as each other. Accordingly, excessive addition of ruthenium to the platinum-containing electrode is not effective in enhancing the activity for oxygen reduction. As has been seen in Fig. 5, the electrode prepared from the amorphous Ni-40Zr-3Pd alloy shows a low Tafel slope and a high activity for oxygen reduction. However, substitution of ruthenium for palladium is detrimental. Hence, the addition of

ruthenium is effective in enhancing the activity of the platinum-containing electrodes for oxygen reduction, but is detrimental for the activity of other electrodes.

The usefulness of the electrode can be evaluated from the difference in the limiting current per mole of platinum group elements contained in the electrode. The effect of the change in the catalyst on the limiting current has not so far been discussed, although the relationship between the limiting current and the specific shape of porous gas-diffusion electrode has been extensively examined [1-8, 19]. It has been reported [19] that the current-limiting factors for oxygen reduction in porous gas-diffusion electrodes are the gas permeability of the gas-side layer and the wettability of the catalyst layer. The current density for oxygen reduction at a constant potential above and below about 0.8 V (NHE) in 105 wt % H_3PO_4 at 190°C is known to be proportional to the platinum content in the catalyst layer and its square root, respectively [5]. The Tafel slope for electrochemical oxygen reduction became twice as high as that of ordinary porous gas-diffusion electrodes [6], when the wettability toward phosphoric acid electrolyte was high. Accordingly, there is an optimal content of PTFE in the porous gas-diffusion electrode to provide an adequate hydrophobicity (wettability) [6].

In the present work the weight ratio of the catalyst powder, carbon black powder, PTFE dispersion and sucrose was fixed at 7:3:3:10. Hence, the difference in the activities of the electrodes is not based on differences in the catalyst content and hydrophobicity of the electrodes. It can, therefore, be said that the difference in the limiting current per mole of platinum group element contained in the electrode shows the difference in the efficiencies of the platinum group elements contained in the catalyst alloy powders. In other words, the fact that the higher activity of the platinum-containing amorphous alloy electrodes compared with that of the platinum black electrode for oxygen reduction indicates that the alloy catalysts are superior to the single platinum metal catalyst, although the fine particle size of the alloy catalysts may also be effective.

The relatively high overvoltage and large Tafel slope suggest that oxygen reduction is the most difficult process for utilization of the hydrogen-oxygen fuel cell at ambient temperature. This is due to the fact that reduction of oxygen does not occur via a monoatomic intermediate but through a polyatomic intermediate, such as O_2H [15, 20].

3.2.3. Oxidation of hydrogen. Figure 7 shows typical examples of polarization curves for hydrogen oxidation. Hydrogen was oxidized by all the electrodes examined at a potential very close to the equilibrium potential. The current measurable by the potentiostat used was 1 A, and hence polarization was stopped when the current reached this value. The current for hydrogen oxidation increases quite sharply with slight polarization because of a high exchange current, i_0 , and then approaches the limiting current asymptotically.

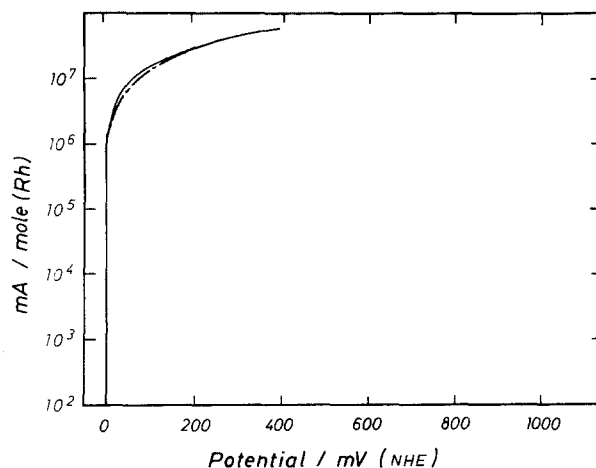


Fig. 7. Potentiodynamic polarization curves of the electrodes prepared from the amorphous Ni-40Zr- x Rh alloys containing 1-3 at % of rhodium for hydrogen oxidation measured in 1 M H_2SO_4 at 25°C with passage of hydrogen in the gas compartment. (—) $x = 1$, (---) $x = 3$, (- - -) $x = 5$.

totically. This fact was observed for all the electrodes examined.

Figure 8 compares polarization curves for electrodes containing different platinum group elements. The platinum- and rhodium-containing electrodes exhibit higher limiting currents than that of the platinum black electrode. The ruthenium-containing electrode also shows a high activity for hydrogen oxidation, but the current for hydrogen oxidation at high potentials tends to decrease, possibly due to dissolution of the less corrosion resistant ruthenium-containing catalyst in the sulphuric acid.

The peculiar behaviour of ruthenium- and palladium-containing amorphous alloy electrodes can be seen by linear plots of currents for hydrogen oxidation as shown in Fig. 9. The current of the ruthenium-containing electrode for hydrogen oxidation at high potentials tends to decrease, possibly due to the anodic dissolution of the ruthenium-containing catalyst having low corrosion resistance. The parabolic increase in the current on the

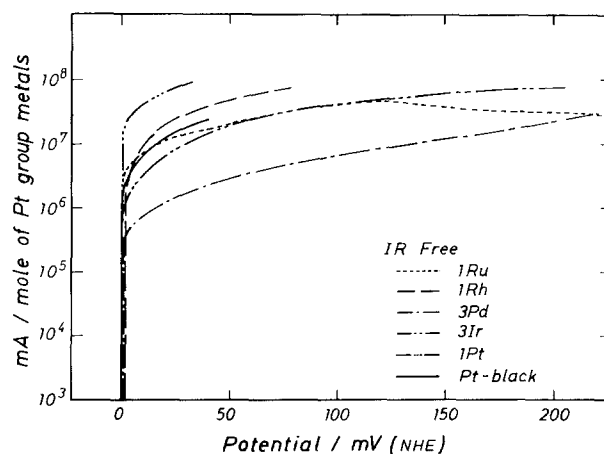


Fig. 8. Potentiodynamic polarization curves of the electrodes prepared from the amorphous Ni-40Zr alloys containing different platinum group elements (xM) for hydrogen oxidation measured in 1 M H_2SO_4 at 25°C with passage of hydrogen in the gas compartment. Corrections for ohmic drop were made.

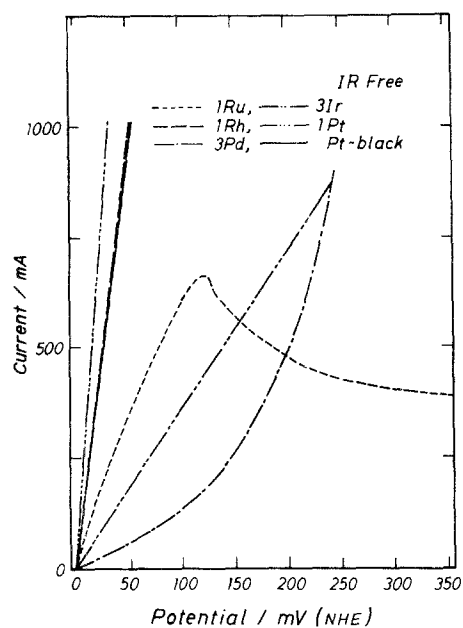


Fig. 9. Linear plots of potentiodynamic polarization curves of the electrodes prepared from the amorphous Ni-40Zr alloys containing different platinum group elements (xM) for hydrogen oxidation measured in 1 M H_2SO_4 with passage of hydrogen in the gas compartment. Corrections for ohmic drop were made.

palladium-containing electrode appears to be due to subtraction of the current for cathodic reduction of palladium oxide from that for oxidation of hydrogen at low potentials.

As shown in Fig. 10, when two kinds of platinum group elements such as platinum and ruthenium or platinum and rhodium are contained, the electrodes have higher activities for hydrogen oxidation in comparison with the platinum black electrode. In particular, the activity of the electrode prepared from the amorphous Ni-40Zr-1.5Ru-1.5Pt alloy is higher than that of the electrode prepared from the amorphous Ni-40Zr-3Pt alloy, in spite of the fact that the activity of the electrodes prepared from the amorphous Ni-40Zr-Ru alloys is not particularly high. Accordingly, substitution of ruthenium for platinum up to a

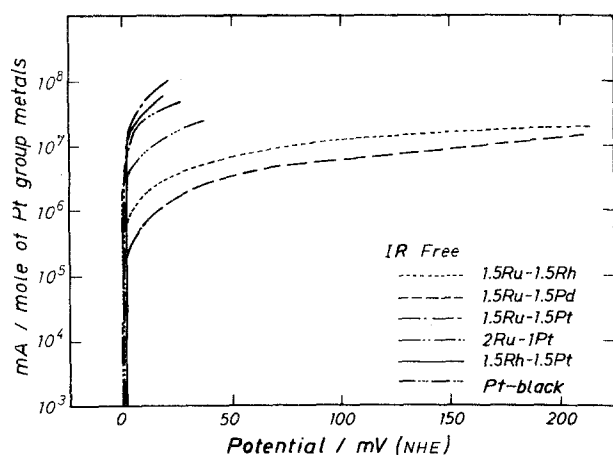


Fig. 10. Potentiodynamic polarization curves of the electrodes prepared from the amorphous Ni-40Zr alloys containing different sets of two kinds of platinum group elements ($xM_1 - yM_2$) for hydrogen oxidation measured in 1 M H_2SO_4 at 25°C with passage of hydrogen in the gas compartment. Corrections for ohmic drop were made.

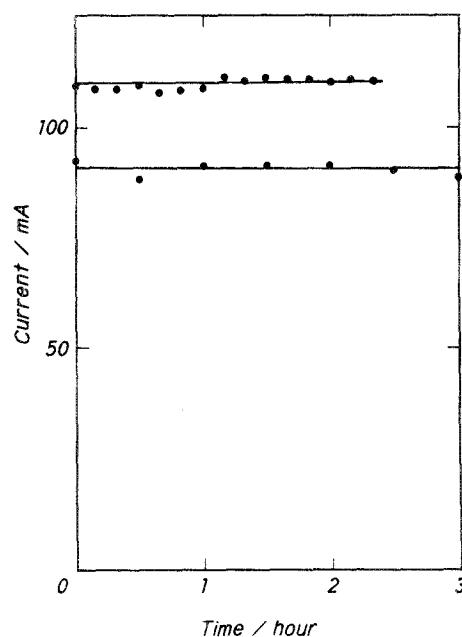


Fig. 11. Change in currents during potentiostatic polarization of the electrodes in 10 mm diameter prepared from the amorphous Ni-40Zr-1Pt (bottom line) and Ni-40Zr-1.5Ru-1.5Pt (top line) alloys for hydrogen oxidation measured in 1 M H_2SO_4 at 25°C with passage of hydrogen in the gas compartment. Taken at -200 mV (SCE) with corrections for ohmic drop were made.

half of the platinum in the amorphous alloy enhances synergistically the catalytic activity for electrochemical oxidation of hydrogen. Although the activity of the electrode prepared from the amorphous Ni-40Zr-Rh alloy is high, the combined addition of platinum and rhodium is not effective in enhancing the catalytic activity. This indicates that the combined addition of platinum and rhodium has no synergistic effect. Substitution of ruthenium for rhodium is clearly detrimental, and hence the combined addition of ruthenium and rhodium has no synergistic effect, but is rather less effective in comparison with rhodium addition.

When ruthenium or palladium was contained, the electrodes prepared from the amorphous Ni-40Ti alloys showed rather higher activity for hydrogen oxidation in comparison with the electrodes prepared from the Ni-40Zr alloys. However, when platinum or rhodium was contained, the difference between the effects of titanium and zirconium was not appreciable.

It has been reported [11] that the platinum-containing amorphous alloy electrode has high activity for oxygen reduction for prolonged times, while the activity of the platinum black electrode for oxygen reduction decreases rapidly. Figure 11 shows currents for hydrogen oxidation observed during potentiostatic polarization. As far as hydrogen oxidation is concerned, no sign of a decrease in current is observed with prolonged polarization. Consequently, the high activities of the amorphous alloy electrodes have been maintained for prolonged oxidation of hydrogen.

It can be said that, because i_0 for a finely dispersed powder catalyst electrode is very high, and because the hydrophobicity of the porous gas-diffusion electrode

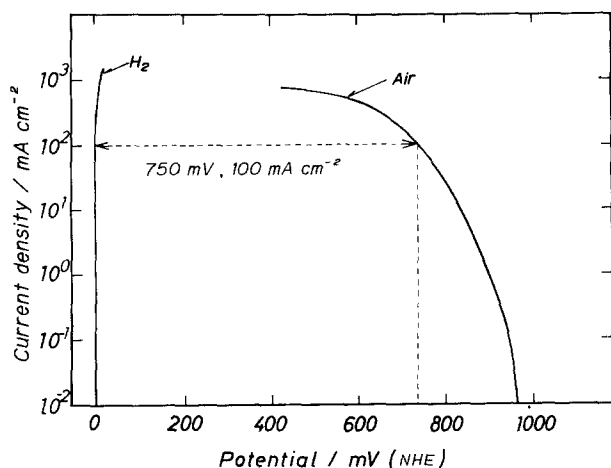


Fig. 12. Polarization curves of the porous gas-diffusion electrode prepared from the amorphous Ni-40Zr-1.5Ru-1.5Pt alloy for hydrogen oxidation and oxygen reduction in 1 M H₂SO₄ at 25°C. Corrections for ohmic drop were made.

is sufficiently high to supply hydrogen to the electrolyte film covering the catalyst, a slight polarization immediately results in the limiting current of diffusion of hydrogen through the electrolyte film. Consequently, hydrogen oxidation is not limiting factor in hydrogen-oxygen fuel cells.

Fig. 12 shows polarization curves when 1 cm² porous gas-diffusion electrodes prepared from the amorphous Ni-40Zr-1.5Ru-1.5Pt alloy are used for both hydrogen oxidation and oxygen reduction. If the temperature of 25°C is taken into account, this is a reasonably efficient fuel cell.

4. Conclusions

Powder catalysts were obtained from amorphous Ni-40Zr and Ni-40Ti alloys containing a few atomic percent of platinum group elements by immersion in 46% HF. The HF immersion gave rise to preferential dissolution of the valve metal and nickel and to the formation of powder catalysts of platinum group metal-base alloys containing some nickel and valve metal. The average diameter of the catalyst powders was 2–3 nm. Porous gas-diffusion electrodes were prepared from these catalysts and polytetrafluoroethylene.

These amorphous alloy electrodes were used for electrochemical reduction of oxygen and oxidation of hydrogen in 1 M H₂SO₄ at 25°C. The platinum-containing electrodes showed overvoltages as low as 250 mV for oxygen reduction. Among them the amorphous alloy electrodes containing Pt-Ru, Pt-Rh,

Pt or Pd showed higher activities than that of the platinum black electrode for oxygen reduction.

Oxidation of hydrogen occurred readily close to the equilibrium potential with almost no overvoltage. Because these electrodes possessed very high activities for oxidation of hydrogen, and because the hydrophobicity of the porous gas-diffusion electrode was sufficiently high to supply hydrogen to the electrolyte film covering the catalyst, these electrodes showed very high exchange currents, and only slight polarization resulted in the limiting currents. The activity of the amorphous alloy electrodes containing Pt-Ru, Pt-Rh or Pt was higher than that of the platinum black electrode for hydrogen oxidation.

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