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The Electrocatalytic Oxidation of Ethylene and Methane, and Reduction of Oxygen on Gas-Diffusion Electrodes Made of Amorphous Nickel-Valve Metal-Platinum Group Metal Alloys*

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Synopsis

Exploratory work has been done on the performance of electrocatalytic reduction of oxygen and anodic oxidation of ethylene and methane on the gas-diffusion electrodes prepared from amorphous alloys containing one atomic percent platinum group elements. Gas-diffusion electrodes were made by coating the mixture of catalysts prepared by immersion in 46% HF from melt-spun ribbon shaped amorphous alloys, carbon black, polytetrafluoroethylene and sugar, and subsequent baking in nitrogen gas. The electrode made of catalyst prepared from amorphous nickel-niobium alloy containing platinum and ruthenium was the most active for electrocatalytic reduction of oxygen. For electro-oxidation of ethylene and methane, amorphous nickel-valve metal alloy containing only platinum possesses higher activity in comparison to the electrode made of platinum black powder.

I. Introduction

Fuel cells which employ hydrocarbon fuels such as town and natural gases are very desirable especially when we construct small scale electric power sources at any location. The development of town gas fuel cells requires effective catalysts for electrochemical oxidation of the gas constituents. Hydrogen, methane and ethylene are major constituents of the town and natural gases.

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Besides having the high corrosion resistance, amorphous alloys have the potential for providing new catalysts or precursors of new catalysts in special reactions. Amorphous alloys are capable of forming a homogeneous solid solution super-saturated with various elements in addition to the synergistic effect of different elements.

It was reported in our previous papers[1,2] that after ribbon-shaped amorphous nickel-valve metal alloys containing a few atomic percent of platinum and other elements were immersed in HF solution, their surfaces became excellent electro-catalysts for chlorine production and for oxidation of methanol. The activation of these alloys is based on the selective dissolution of electrocatalytically less active valve metals and nickel with a consequent accumulation of electrocatalytically active platinum group elements in the surface layer. Furthermore, it was found that prolonged immersion of these amorphous alloys in HF solution resulted in the formation of powder consisting of platinum group elements and a little nickel and valve metals[1,3]. When porous gas-diffusion electrode was made of these powders prepared from amorphous alloys, the electrode showed excellent performance for oxidation of hydrogen, methanol and reduction of oxygen in sulfuric acid at ambient temperature[4,5].

The present work is attempted to qualify the performance of porous gas-diffusion electrodes consisting of powder catalysts prepared from amorphous nickel-valve metal alloys containing small amounts of platinum group metals and other elements in electro-oxidation of ethylene and methane, and electro-reduction of oxygen in sulfuric acid at ambient temperature.

II. Experimental

Alloy ingots were prepared by arc or induction melting of commercial metals under an argon atmosphere. The alloys were then melt-spun in argon into ribbons approximately 1 mm wide and 30 μm thick. They were Ni-Ti, Ni-Zr, Ni-Nb and Ni-Ta alloys containing Ru, Rh, Pd, Ir, Pt, Pt-Ru, Pt-Rh, Pt-Pd, Pt-Ir, Pd-Ru, Pd-Rh, and Pd-Ir. The amorphous nature of the alloys was confirmed by X-ray diffraction with Cu K_{α} radiation. The amorphous alloy ribbons thus prepared were immersed in 46% HF solution at ambient temperature until hydrogen gas evolution was stopped. The resulting mass was filtered, washed repeatedly with distilled water and finally air dried. By this treatment, black catalyst powders were obtained. The composition of the powder catalysts was determined by electron probe micro-analysis and their structure was examined by X-ray diffraction at θ - 2θ mode with Cu K_{α} radiation. The size of the catalyst powder was estimated from the full width at half maximum of the X-ray diffraction pattern.

The porous gas-diffusion electrodes were synthesized by a method similar to that described in previous papers[4,5]. The materials used for the preparation of the electrodes were the catalyst powders, carbon black (Toka black #5500), PTFE (Mitsui fluoro chemical Co., 30-J), sugar and a carbon paper (Kureha E315) as the current collector. The weight ratios of the catalyst powder, carbon black powder, PTFE and sugar were mainly 7:3:3:10 and 3:3:4:0 for oxygen reduction and ethylene oxidation, and methane oxidation, respectively. But it was sometimes varied to change the concentration of catalyst. 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. The thickness of the catalyst layer of the electrode was about 0.05 mm.

Figure 1 shows the schematic drawing of an electrolytic cell used for the examination of the electrode characteristics. The reaction side of the electrode, 8.8 mm diameter, is exposed to the electrolyte and the other side is exposed to air, ethylene or methane. The electrolyte used was deoxygenated 1M H₂SO₄ at 25 °C. The saturated calomel electrode and platinum gauge were used as reference and counter electrodes, respectively. Cyclic voltammetry was carried out for activation of the electrode in the sulfuric acid at a potential sweep rate of 50 mV/s in the potential range from -0.25 to 1.35V (SCE) with oxygen free nitrogen passing

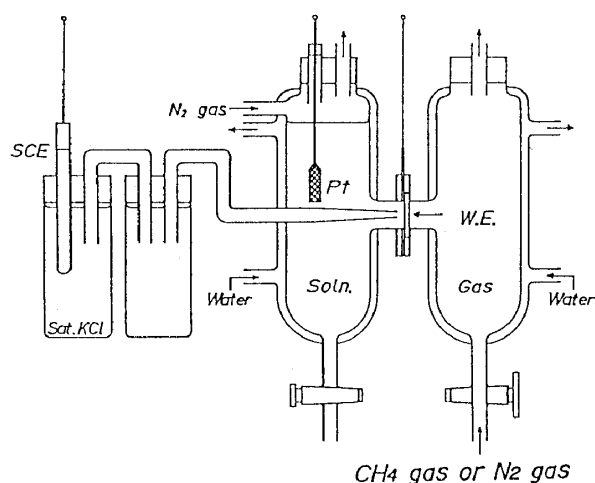


Figure 1 Schematic arrangement of the electrolysis cell.

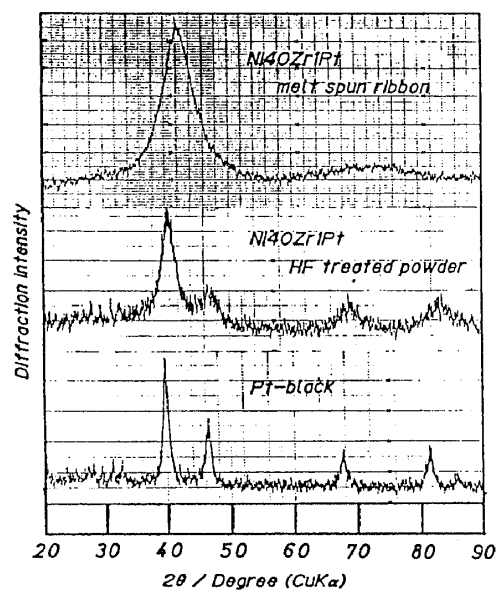


Figure 2 X-ray diffraction patterns of amorphous Ni-40Zr-1Pt alloy ribbons and HF-treated powders.

through the gas compartment. Subsequently, the electrode performance for oxygen reduction, and ethylene and methane oxidation was potentiodynamically examined with a potential sweep rate of 50 mV/min by passing air, ethylene or methane gas stream through gas compartment, respectively.

III. Results

1. Characterization of powder catalysts

Figure 2 shows typical X-ray diffraction patterns of melt-spun ribbon and catalyst powder by HF-treatment of Ni-40Zr-1Pt alloy together with diffraction pattern of platinum black for comparison. Catalyst powder shows the broad diffraction patterns of the fcc phase, although the lattice constant of the catalyst powder ($a_0=0.3825$ nm) is smaller than that of platinum black ($a_0=0.392$ nm). The particle size of the catalyst estimated from full width at half maxima of 111 and 222 reflections was about 2.6 nm, while that of the platinum black was about 7.3 nm. 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 single platinum group metals. When the amorphous alloys contained ruthenium, the catalyst powders 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 hcp ruthenium.

Table 1 shows the composition of the catalyst powder determined by EPMA and the size of catalyst powder estimated from X-ray diffraction patterns. This shows that the HF treatment results in a remarkable enrichment of platinum group elements as a results of preferential dissolution of iron group elements and valve metals. Although platinum group elements contained in the amorphous alloys was only one atomic percent, they accumulated to more than 55 atomic percent. It is to be noted that, when two kinds of platinum 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 alloys. The catalyst powders used consist of fine grains of about 2-4 nm, irrespective of platinum group elements and of their contents, while the particle size of the platinum black is about 7 nm.

Therefore, HF-treatment led to preferential dissolution of the valve metal and iron-group elements with a consequent formation of microcrystalline alloy powders consisting of concentrated platinum group elements and some iron-group elements and valve metals.

2. Electrode performance

2.1 Performance of oxygen-reducing electrodes

Figure 3 shows the potentiodynamic polarization curves for oxygen reduction on gas-diffusion electrodes prepared from amorphous Ni-40Nb-1M alloys containing different platinum group elements, together with data for platinum black electrode. From a practical point of view, the current densities are presented in terms of amperes per gram of catalysts. From this figure it is apparent that increasing order of the oxygen reduction activity of the amorphous alloy electrodes is almost the same as the decreasing order of the overvoltage for oxygen reduction, that is ruthenium < iridium < rhodium < palladium < platinum. But the platinum containing amorphous alloy electrode is not superior to the platinum black electrode. The sharp current increase for ruthenium containing alloy electrode close to open circuit potential is probably due to reduction of oxide during previous cyclic voltammetry.

In order to obtain more active catalysts, combined addition of two kinds of platinum group elements were attempted. Figures 4 and 5 show the potentiodynamic polarization curves for oxygen reduction on gas-diffusion electrodes prepared from amorphous Ni-40Nb-0.5Pt-0.5(Ru, Pd, Ir, Rh) and Ni-40Nb-0.5Pd-0.5(Ru, Ir or Rh), respectively. Included in these figures is the polarization curve of platinum black electrode. The combined addition of platinum and ruthenium, palladium or rhodium decreases the apparent Tafel slope. Particularly, Ni-40Nb-0.5Pt-0.5Ru alloy electrode shows the highest activity, which is higher than that for platinum black electrode. However, the replacement of a part of palladium with ruthenium, rhodium or iridium is not effective for improving the activity, although combined addition of palladium and ruthenium or palladium and rhodium decreases the Tafel slope in comparison with the amorphous Ni-40Nb-1Pd alloy electrode.

2.2 Performance of ethylene oxidation

Experiments were run either in the absence (blanks, N_2) or in the presence of ethylene under 1 atm. Figure 6 shows the potentiodynamic potential/current profiles for electro-oxidation of ethylene on gas-diffusion electrodes prepared from amorphous Ni-40Nb-1M alloys, M=Ru, Rh, Pd, Ir or Pt. The oxidation currents were obtained by subtracting blanks (N_2) from those measured in the presence of ethylene. The platinum-containing amorphous alloy electrode only shows higher activity in the whole potential region than the platinum black electrode. In the case of Ru, Rh or Pd-containing alloys, the overvoltage for oxidation of ethylene is higher than platinum black, although Ru, Rh and Pd are acting as promoters in the high potential region.

Combined addition of platinum group elements did not improve the catalytic activity. Figures 7 and 8 depict potentiodynamic polarization curves for ethylene

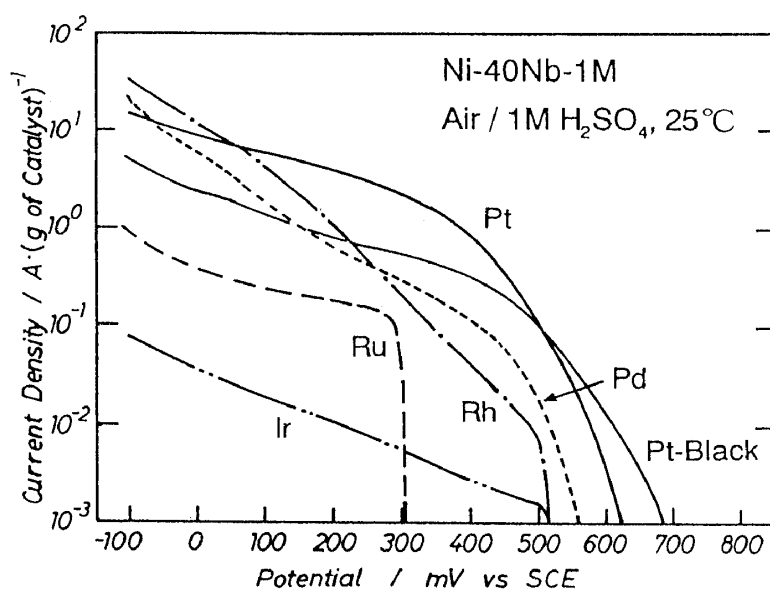


Figure 3 Potentiodynamic polarization curves of the gas-diffusion electrodes prepared from Ni-40Nb-1M alloys, M=Ru, Rh, Pd, Ir or Pt for oxygen reduction measured in 1M H₂SO₄ at 25 °C with passage of air in the gas compartment.

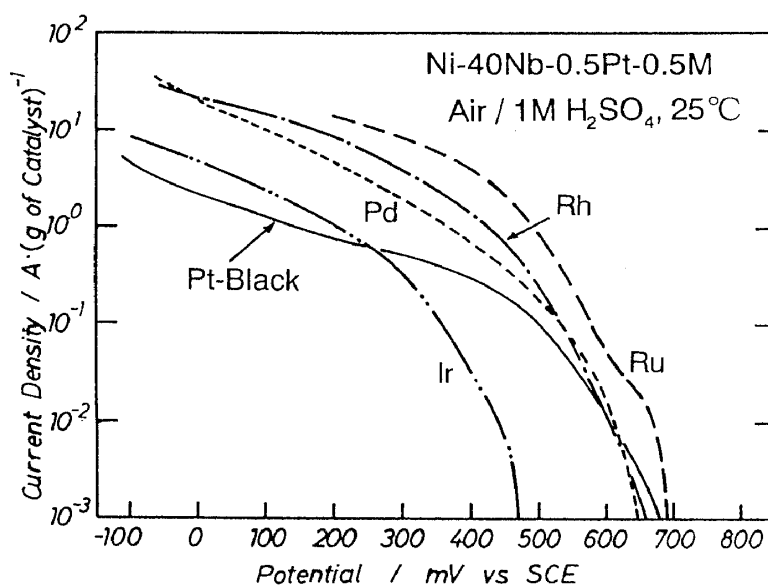


Figure 4 Potentiodynamic polarization curves of the gas-diffusion electrodes prepared from Ni-40Nb-0.5Pt-0.5M alloys, M = Ru, Rh, Pd, or Ir for oxygen reduction measured in 1M H₂SO₄ at 25 °C with passage of air in the gas compartment.

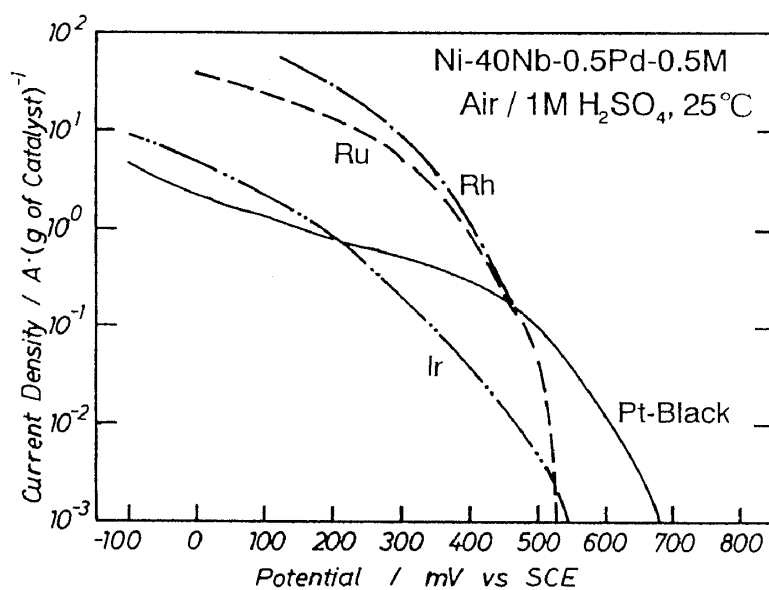


Figure 5 Potentiodynamic polarization curves of the gas-diffusion electrodes prepared from Ni-40Nb-0.5Pd-0.5M alloys, M = Ru, Rh, or Ir for oxygen reduction measured in 1M H₂SO₄ at 25 °C with passage of air in the gas compartment.

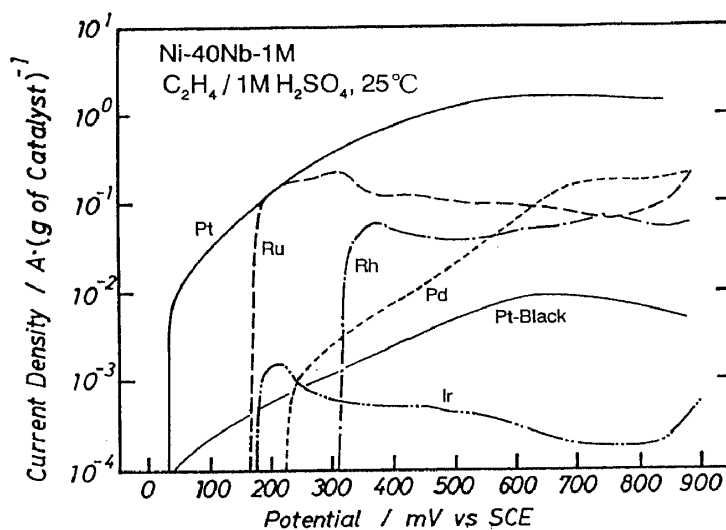


Figure 6 Potentiodynamic polarization curves of the gas-diffusion electrodes prepared from Ni-40Nb-1M alloys, M = Ru, Rh, Pd, Ir or Pt for ethylene oxidation measured in 1M H₂SO₄ at 25 °C with passage of ethylene in the gas compartment.

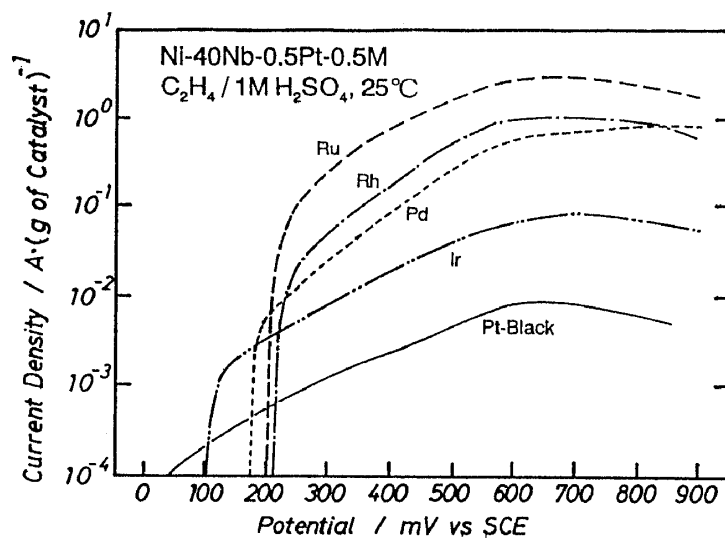


Figure 7 Potentiodynamic polarization curves of the gas-diffusion electrodes prepared from Ni-40Nb-0.5Pt-0.5M alloys, M = Ru, Rh, Pd or Ir for ethylene oxidation measured in 1M H₂SO₄ at 25 °C with passage of ethylene in the gas compartment.

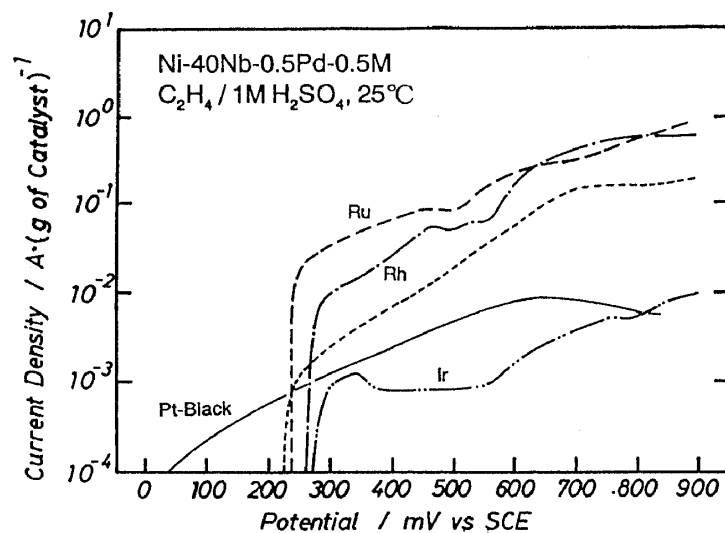


Figure 8 Potentiodynamic polarization curves of the gas-diffusion electrodes prepared from Ni-40Nb-0.5Pd-0.5M alloys, M = Ru, Rh or Ir for ethylene oxidation measured in 1M H₂SO₄ at 25 °C with passage of ethylene in the gas compartment.

oxidation on gas-diffusion electrodes prepared from amorphous Ni-40Nb-0.5Pt-0.5(Ru, Rh, Pd or Ir) and Ni-40Nb-0.5Pd-0.5(Ru, Rh or Ir) alloys, respectively. Compared with the platinum black electrode, the ethylene oxidation overvoltages of these alloy electrodes are higher, although their oxidation current densities are higher in the high potential region. Consequently, it is unlikely that the substitution of a part of platinum or palladium with other platinum group elements would cause improvement in the activity for ethylene oxidation.

2.3 Performance of methane oxidation

Figure 9 shows the potentiodynamic potential/current profiles for electro-oxidation of methane on gas-diffusion electrodes prepared from amorphous Ni-40Zr-1Pt alloy together with platinum black electrode. Experiments were carried out similar to ethylene oxidation. In the case of the platinum black electrode, the oxidation current density is almost the same as that measured in N₂ gas, indicating no particular enhancement in the oxidation of methane by the platinum black electrode. On the other hand, the amorphous alloy electrode gives enhanced activity for oxidation of methane, although the current density is low as compared with ethylene oxidation and the overvoltage is very high. The change of valve metal from zirconium to titanium led to change in the oxidation behavior. Zirconium or tantalum-containing alloy electrode has higher oxidation activity as compared with titanium and niobium-containing alloys. An attempt was also made to compare the catalytic activity for iron-, cobalt- and nickel-base amorphous alloy electrodes. The nickel-base amorphous alloy electrode showed the highest activity. Therefore, nickel-zirconium amorphous alloys were employed for oxidation of methane.

Figure 10 summarizes the relation between net oxidation current density at 650 mV (SCE) as well as the overvoltage for methane oxidation and the alloy bulk composition of Ni-40Zr alloys containing one and two kinds of platinum group elements. The amorphous Ni-40Zr-1M alloy containing Pt or Pd has relatively high activity. However, combined addition of platinum group elements are detrimental for electro-oxidation of methane. No synergistic effect between platinum and other platinum group elements was indicated in this reaction.

IV. Discussion

In this work, the better catalytic performance was observed for ethylene oxidation than methane oxidation in sulfuric acid on any electrodes. These observations are in agreement with expectations based on the studies of hydrocarbon adsorption on platinum. The alkenes, which adsorb rapidly and to a large extent on platinum, can support higher current density than can the corresponding alkanes in

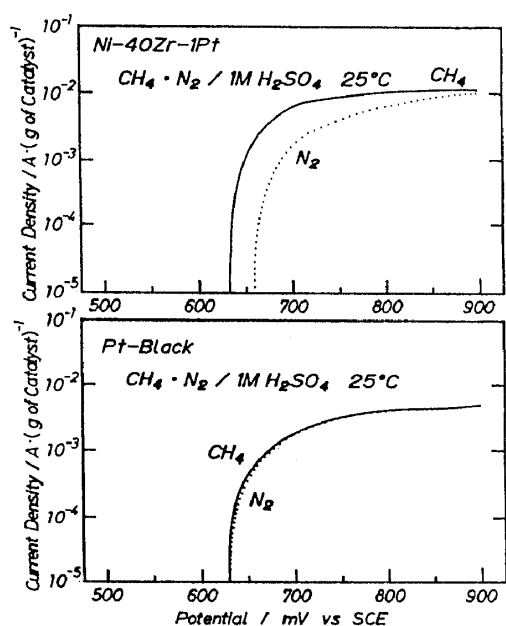


Figure 9 Potentiodynamic polarization curves of the gas-diffusion electrodes prepared from Ni-40Zr-1Pt alloy and platinum black for methane oxidation measured in 1M H₂SO₄ at 25 °C.

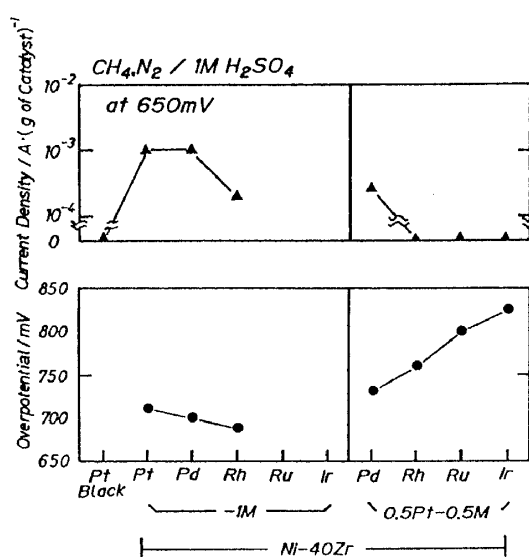


Figure 10 Anodic current densities and overvoltages of gas-diffusion electrodes prepared from amorphous Ni-40Zr-1M alloys containing platinum group element.

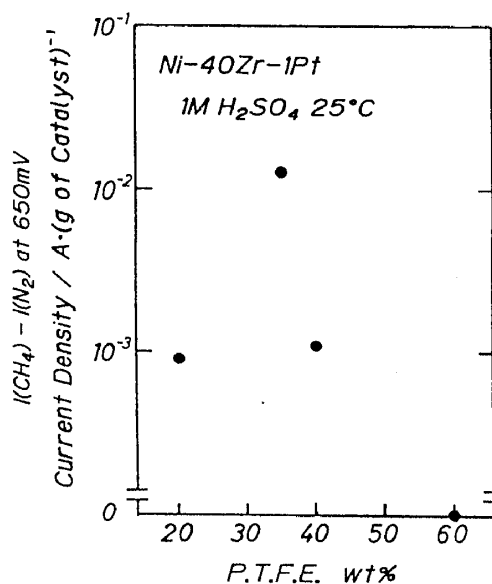


Figure 11 Change in anodic oxidation current densities of methane for the electrodes prepared from amorphous Ni-40Zr-1Pt alloy as a function of PTFE content.

acid electrolytes at low temperature (below about 80 °C)[6]. It was also found that methane was adsorbed only very slowly and to a very small extent[7]. More than one hour was required for the open circuit potential to reach a steady state value, when methane was adsorbed on platinized platinum in 1 N H₂SO₄ at temperatures in the range of 25–95 °C ; the amount of adsorption of methane corresponded to only 10 μC/cm² at 25 °C and 34 μC/cm² at 80 °C, as obtained from galvanostatic oxidation in the range of 0.35–0.7 V (NHE)[8]. By contrast, ethylene adsorbed very rapidly onto smooth platinum in 1 N HClO₄ at 30 °C[9]. Adsorption at 0.4 V yielded a coverage on smooth platinum in 1N HClO₄ at 30 °C of 460 μC/cm². Therefore, ethylene is an attractive fuel for fuel cell with respect to catalytic activity.

As shown in Figs. 6–10, only platinum of the alloying elements in amorphous alloys has significant activity for anodic oxidation of ethylene and methane. No synergistic effect between platinum and other platinum group elements was indicated in these reactions. Several investigators have observed that the activity of platinum for the oxidation of alkanes in strong acid electrolyte is orders of magnitude greater than that of any other platinoid element[10–12]. Furthermore, Grubb[13] examined 29 elements for activity toward oxidation of hydrocarbons in KOH or H₂SO₄ electrolytes at 65 °C and found that only platinum showed any significant level of activity. In our experiments the ratio of platinum to other platinum group elements was fixed at 1:1. The work which changes this ratio needs to be investigated further.

In the case of methane oxidation, even with very small exchange current density and small limiting current density at ambient temperature as shown in Fig.9, a large current density can be obtained if a larger effective surface area of the electrodes can be utilized. Therefore, the effect of PTFE content, which would change hydrophobicity of the electrode, on the oxidation activity of methane was examined. The results were shown in Figure 11. The highest current density obtained with the electrode containing 35 wt% PTFE is about one order of magnitude greater than that obtained with the electrode of 40 wt% PTFE which was used in Fig. 10. Consequently, the structure of the electrode can have a great influence on catalyst performance.

V. Conclusions

The performance of gas-diffusion electrodes prepared from amorphous alloys for reduction of oxygen, and electro-oxidation of ethylene and methane was examined in 1 M H₂SO₄ at 25 °C.

Powder catalysts were prepared from amorphous nickel-valve metal alloys

containing only one at% platinum group elements by immersion in 46% HF. This treatment led to preferential dissolution of valve metals and nickel with a consequent formation of microcrystalline alloy powders consisting of concentrated platinum group elements. A dough was produced by mixing the powder catalysts, carbon black powder, filler material and PTFE, and this was rolled to a carbon paper. The porous gas-diffusion electrodes were obtained by heating in nitrogen atmosphere.

The electrode made of catalysts prepared from amorphous nickel-valve metal alloy containing platinum group metals exhibited high catalytic activities. Some of these electrodes have higher activity in comparison to the electrode made of platinum black; that is, they are Ni-40Nb-0.5Pt-0.5Ru alloy electrode for oxygen reduction, and Ni-40Nb-1Pt and Ni-40Zr-1Pt alloy electrodes for electro-oxidation of ethylene and methane, respectively.

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