

Amorphous Ni-Zr-platinum group element alloys
for oxidation of hydrogen

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A key for widespread use of hydrogen-oxygen fuel cell is to decrease greatly the use of platinum group elements in the cell.

Amorphous alloys are known to possess a variety of interesting chemical properties. We found in 1980's that hydrofluoric acid treatment of amorphous Ni-valve metal alloys containing small amounts of platinum group elements was quite effective for production of electrodes for chlorine evolution in seawater electrolysis whose activity was higher than the dimensionally stable anode consisting of ruthenium oxide (1,2). It has been clarified that hydrofluoric acid treatment for amorphous alloys is effective in obtaining catalysts in which platinum group elements are concentrated and finely dispersed in the surface region and act synergistically with other coexisting elements. Furthermore, we prepared gas diffusion electrodes using catalyst powders obtained by hydrofluoric acid treatment for amorphous Ni-valve metal-platinum group metal alloys and examined their performance for oxidation of hydrocarbon fuels. The electrodes were more active than that prepared by platinum black catalysts for oxidation of methanol (3-5), formaldehyde (6), hydrogen (7), ethylene (8-10) and propane (11).

The present work aims to tailor amorphous Ni-Zr-platinum group element alloy catalysts for electro-oxidation of hydrogen in sulfuric acid. Particular attention was paid to the synergistic effect of coexisting elements.

Experiment

Amorphous Ni-40 at%Zr-(2-x)at%Pt-x at%(Ru, Rh, Pd or Rh) alloys were prepared by melt spinning method. Most of experiments were carried out using melt-spun ribbon shaped amorphous alloys whose surface was activated by immersion in 5% HF. For preparation of catalyst powders the amorphous alloy ribbons were immersed in 46% HF at room temperature for about 10 min. The gas diffusion electrodes using the catalyst powders were prepared as follows: The catalysts were mixed with carbon black, PTFE, sucrose and surfactant. The mixture was pasted on a carbon paper, dried at 100°C and finally calcinated at 300°C in nitrogen atmosphere.

In order to clarify the role of individual alloying elements, Ni-50at% platinum group element alloys, Zr-50at% platinum group element alloys, Ni-30at%Pt-30at% other platinum group element alloys and Zr-30at%Pt-30at% other platinum group element alloys prepared by Ar arc melting were also used in addition to platinum group metals and platinized platinum.

The electrolyte used was deaerated 1M H₂SO₄ at 30°C. The electrochemical performance was potentiodynamically examined in the hydrogen-saturated sulfuric acid.

The characterization of electrode surface was performed by X-ray photoelectron spectroscopy. The binding energies of the photoelectrons were calibrated by a method described elsewhere (12,13): the binding energies of the Au 4f_{7/2} and 4f_{5/2} electrons of pure gold and

the Cu 2p_{3/2} electrons of pure copper were taken as 84.07, 87.74 and 932.53 eV, respectively, and the kinetic energy of Cu L_{4,5}M_{4,5}M_{4,5} Auger electrons of pure copper as 918.65 eV.

Results and discussion

All electrodes prepared from amorphous quaternary Ni-40Zr-(2-x)Pt-xM alloys, where M is platinum group element other than platinum, showed significantly higher activity for oxidation of hydrogen in comparison with those prepared from amorphous ternary Ni-40Zr alloys containing 2at% platinum group elements. The activities of electrode obtained from the quaternary alloys for oxidation of hydrogen were some ten to several tens of times as high as that of platinized platinum.

Examination of the role of individual elements gave the following results:

Platinum group metals and binary Pt alloys with other platinum group elements were not sufficiently active for oxidation of hydrogen, while Zr alloys with platinum group elements showed orders of magnitude higher activity for oxidation of hydrogen.

An XPS study revealed that charge transfer occurred from platinum and zirconium to ruthenium, rhodium, palladium, iridium and nickel in the alloys. The charge transfer from platinum and zirconium may enhance the electron transfer from hydrogen to the electrodes.

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