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Life Tests of Carbon-Supported Pt-Cr-Cu Electrocatalysts in Solid-Polymer Fuel Cells

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ABSTRACT

The life tests, at 100 and 200 mA/cm² in a solid-polymer fuel cell, indicate that the Pt-Cr-Cu/C catalyst is relatively more active than the Pt/C catalyst even after operating the cell for 300 h. The elemental analyses of the anode and cathode catalysts, before and after the stability test, indicate an excessive loss of copper from the cathode. The enhanced activity of this catalyst is explained in terms of its improved wetting of the catalyst particles and of the Raney-type Pt-Cr-Cu alloy formation.

Solid-polymer fuel cells (SPFCs) are usually operated at relatively low temperatures (80 to 100°C) due to drying out of the polymer membrane at higher temperatures. Because of these low operating temperatures and the sluggish oxygen reduction reaction, these fuel cells are usually operated with platinum electrodes. The effective utilization of platinum is necessary because of the high cost and the relatively limited abundance of this metal. Recently, low-platinum-loaded electrodes in SPFCs have been demonstrated with a three-dimensional reaction zone by impregnating Nafion into the active layers of the carbon-supported platinum electrodes.¹⁻³ A further decrease of the platinum loading could be achieved by employing more active platinum-alloy electrocatalysts instead of platinum alone.⁴ In our previous paper,⁵ we showed an enhanced activity for the Pt-Cr-Cu electrocatalyst, compared to Pt and Pt-Cr alloy electrocatalysts. This electrocatalyst contained a mixture of Pt-Cr-Cu alloy, copper metal, and copper oxide.

The stability and hence the activity of this material is questionable because of the unstable nature of copper under the operating fuel cell conditions. Here, we present data to show that this material is more active as compared to platinum alone even after a prolonged operation of the cell at 200 mA/cm².

Experimental

Standard 20 weight percent (w/o) Pt/C electrode (0.35 mg/cm² Pt loading, ETEK, Natick, MA) impregnated with Nafion (ca. 1 mg/cm²) was used as the anode (5 cm² geometric surface area) in SPFC.

Carbon-supported Pt or Pt-Cr-Cu, prepared in our laboratory, was used as the cathode catalyst. Carbon-supported Pt powder (ca. 10 w/o Pt/C) was prepared, from carbon black (Vulcan XC-72, Cabot Corporation) and dinitrodiammineplatinum(II) complex, by heating at 900°C for 1 h in a flowing nitrogen atmosphere. Carbon-supported Pt-Cr-Cu powder was prepared as follows: chromium and copper metals were precipitated on suspended Pt/C powders (from solutions containing ammonium chromate and copper nitrate), filtered, dried, and heat-treated at 900°C for 1 h in a flowing nitrogen atmosphere to effect alloying. X-ray diffraction studies showed the presence of Pt-Cr-Cu alloy along with copper metal and copper oxide. Transmission electron microscopic (TEM) studies indicated a higher particle size for the Pt-Cr-Cu catalysts (25 to 201 Å) compared to the Pt catalysts (22 to 98 Å). The detailed preparation procedure and characterizations of these electrocata-

lysts can be found elsewhere.⁵ The elemental compositions of the Pt-Cr-Cu catalyst were found to be Pt 28.3 w/o, Cr 16.2 w/o, and Cu 55.5 w/o. This ternary electrocatalyst is designated by Pt-Cr-Cu56/C. Here, the numeral 56 represents the weight percentage of copper in the Pt-Cr-Cu catalyst. A known amount of Pt/C or Pt-Cr-Cu56/C powder was ultrasonically blended in 5 w/o Nafion solution (Aldrich) diluted in 0.3 ml H₂O to obtain a thick catalyst paint. The paint was then coated onto uncatalyzed carbon backing layer (ETEK) of 5 cm² area. The electrode was vacuum dried at 70°C for 1 h. This electrode served as the cathode in SPFC. The Pt loadings in the cathodes were 0.44 and 0.37 mg/cm² for Pt/C and Pt-Cr-Cu56/C catalysts, respectively. The dry Nafion loading in the cathodes was maintained at 2.6 mg/cm². A precleaned Nafion 117 membrane (Aldrich) was then hot-pressed between the electrodes at 150°C and approximately 221 bar for 60 s to obtain a single-cell assembly.

A single-cell test-fixture (GlobeTech, Inc., Bryan, Texas), coupled with a test-station (described in Ref. 5), was used for SPFC tests at 50°C. Hydrogen and oxygen pressures were maintained at 4 and 5 atmospheres, respectively. The iR-corrected polarization tests were carried out using a Princeton Applied Research (PAR) 273 potentiostat. The life tests at 100 and 200 mA/cm² were carried out using a PAR 273 potentiostat and a Hewlett Packard power supply, respectively. After termination of the life tests, the powders scraped from the anode and cathode sides of the membrane were analyzed by energy dispersive x-rays (EDS) and x-ray diffraction (XRD). Elemental composition was determined by a Kevex energy dispersive x-ray spectrometer fit with a Hitachi 2300 scanning electron microscope. X-ray diffractograms were recorded using a Rigaku Rotaflex x-ray diffractometer with a source of copper radiation. The diffractometer was operated in the step-scan mode with a 0.1° step and 3 s fixed time in the range of 30 to 55° (2θ). X-ray photoelectron spectroscopy (XPS) measurements were carried out in a VG ESCALAB MKII apparatus with MgK_α radiation (1253.6 eV). The C_{1s} peak of bulk carbon support at 284.6 eV was used as a reference. The spectra were also recorded after sputter cleaning the sample surface for 30 s with an Ar⁺ ion beam.

Results and Discussion

XPS spectrum of the survey scan for the Pt-Cr-Cu56/C catalyst is shown in Fig. 1A. Examinations of this spectrum indicate the presence of Pt, Cu, O, S, and C. The peak corresponding to Cr was not detected both in the survey scan and the individual window scan. The C peak and S peak are due to the carbon support and

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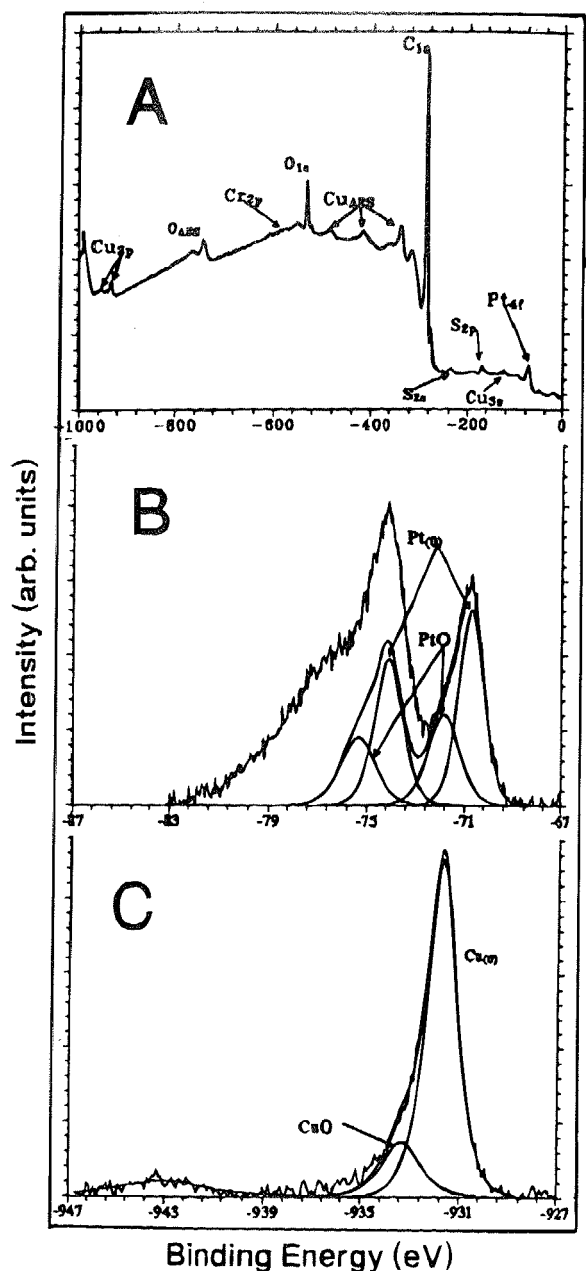


Fig. 1. XPS spectra for Pt-Cr-Cu56/C: (A) the survey scan, (B) the window scan for Pt and, (C) the window scan for Cu (the spectra obtained after the standard curve fitting are also shown for the window scans to indicate the presence of oxides along with the metals).

sulfur contamination in the carbon support, respectively. The XPS spectra of the individual window scans for Pt_{4f} and Cu_{2p} are shown in Fig. 1B and C, respectively. The standard curve fitting displayed the presence of zero-valent Pt and PtO, zero-valent Cu and CuO. Sputter cleaning increased the intensities and areas for the Pt_{4f} and Cu_{2p} peaks, but decreased both for the O_{1s} peak. This shows that the surface oxidation of the catalyst particles probably occurred because of the atmospheric exposure of the sample. X-ray diffraction studies also indicated the presence of copper oxide along with copper metal.⁵

The performance comparison between Pt/C and Pt-Cr-Cu56/C is shown in Fig. 2. These polarization curves were obtained, before starting the life tests, at the cell temperature of 50°C. The enhanced activity of Pt-Cr-Cu56/C as compared to Pt/C may be interpreted in terms of the combined effects of the following: (i) improved wetting of the active catalyst particles by the Nafion solution (during ultrasonic blending of the paint) due to the presence of copper oxide.^{3,6} The wetting process increases the interfacial area between the catalyst particles and the recast Nafion. The cyclic voltammetry

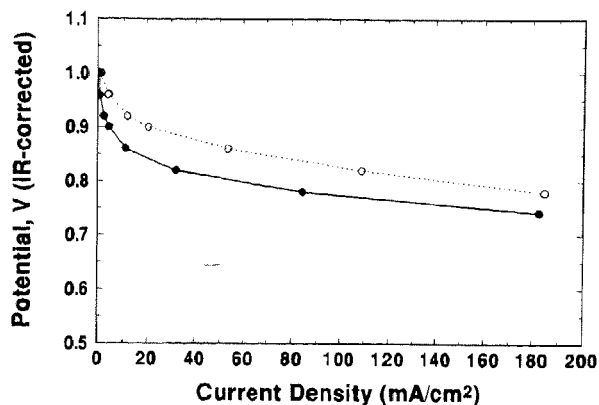


Fig. 2. Oxygen reduction performance for Pt/C (solid line) and Pt-Cr-Cu56/C (dotted line) electrocatalysts at the cell temperature of 50°C.

studies indicated an improved electrochemical area for the Pt-Cr-Cu catalysts as compared to the Pt catalysts,⁵ and (ii) the Raney-type Pt-Cr-Cu alloy formation due to a large dissolution of the base metals or base-metal oxides under operating fuel cell conditions.⁷ This process increases the surface roughening and hence the active area of the Pt-Cr-Cu alloy particles.

A relatively long-term life test was carried out for the Pt-Cr-Cu56/C catalyst at the cell temperature of 50°C. For the purpose of comparison, a short-term life test was also carried out for the Pt/C catalyst. The initial tests were carried out at a current density of 100 mA/cm², and later tests were carried out at a current density of 200 mA/cm². As shown in Fig. 3, a relatively fast decay of about 12 mV was observed for the Pt-Cr-Cu56/C catalyst in the first 10 h of cell operation at a current density of 100 mA/cm². In the next 20 h of cell operation almost no voltage drop was observed. After changing the current density value from 100 to 200 mA/cm², the cell potential slowly reached a steady value of ca. 740 mV in about 16 h of the cell operation. The cell potential stayed nearly constant at 740 ± 5 mV throughout the next 254 h of cell operation. The initial activity may be due to the contributions from both the Raney-type Pt-Cr-Cu alloy (normal adsorption mechanism) and copper/chromium oxide (redox mechanism). The oxide species may act as redox mediators and contribute to the electrocatalytic reduction of oxygen.⁸ The slight degrading performance in the initial period may be due to the loss of assistance from these redox mediators because of the dissolution and migration of these components to the anode side through the membrane (elemental compositional analyses of the anode and cathode are discussed later). Thus the long-term stable performance of the catalyst may largely be due to the Raney-type Pt-Cr-Cu alloy form.

X-ray diffractograms of the Pt/C anode and Pt-Cr-Cu56/C cathode powders, recorded after the life tests, are shown in Fig. 4. Recently, Wilson *et al.*⁹ have reported the x-ray diffractogram for the Nafion-impregnated Pt/C catalyst (ETEK). For the peak at 2θ = 39.8°, the reported shape of the peak profile is symmetric, and the full-width at half-maximum (FWHM) value is 2.84°.

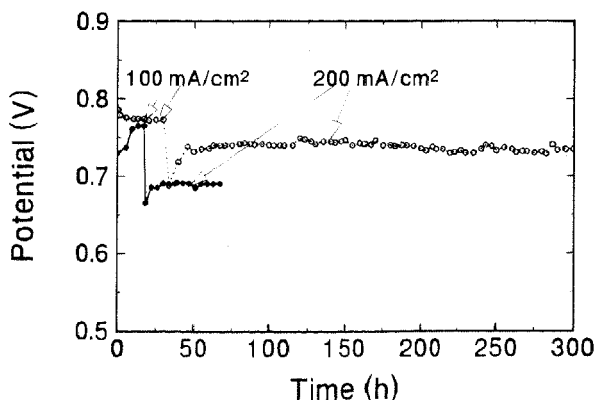


Fig. 3. Life tests of Pt/C (solid line) and Pt-Cr-Cu56/C (dotted line) electrocatalysts for the oxygen reduction reaction at 50°C and at the current densities of 100 and 200 mA/cm².

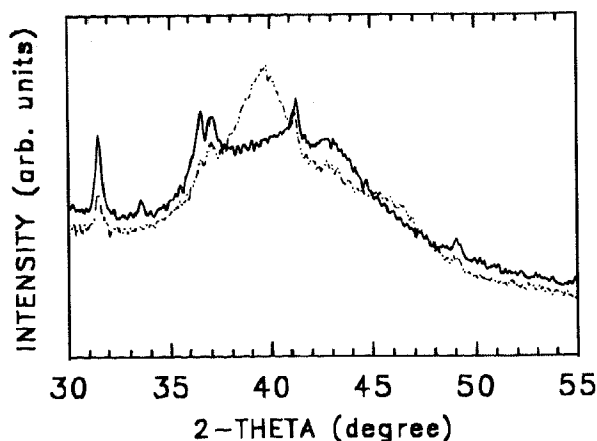


Fig. 4. X-ray diffractograms of the anode (dotted line) and the cathode (solid line) electrocatalysts recorded after 300 h of life tests.

for the Pt/C anode powder of the present study, shown in Fig. 4, is asymmetric, and the FWHM value is much higher than the reported value. These are due to strong overlapping of the diffraction peaks of the recast Nafion. Similar interference is also observed for the cathode powder. Because of this strong interference, no conclusive information is obtained from the XRD studies.

Energy dispersive x-ray studies of the anode powder, after the life test, indicated the presence of Cr and Cu along with Pt. Before the life test, the Pt, Cr, and Cu compositions (w/o) of the cathode powder were 28.3, 16.2, and 55.5, respectively. After the life test, the Pt, Cr, and Cu compositions (w/o) of the cathode powder were 65.7, 29.2, and 5.1, respectively. The overall increase of Pt and Cr compositions, and a large decrease of Cu composition of the cathode powder, after the life test, indicate the excessive loss of Cu from the cathode during the cell operation. These anode and cathode compositional analyses, after the stability test, show that the nonnoble metal components, viz. Cu and Cr, dissolve at the cathode, migrate through the membrane, and deposit on the anode as Cu and Cr metals. The loss of nonnoble metal components including chromium is possible under operating fuel-cell conditions.⁷ These studies coupled with the life tests may indicate that

the major contribution to the long-term activity of this material originates from the Raney-type Pt-Cr-Cu alloy formation.

Conclusion

The Pt-Cr-Cu/C material is more active than Pt/C for the oxygen reduction reaction in SPFCs. A relatively long-term life test at 100 and 200 mA/cm² shows a slight performance loss in the initial 10 h of operation and nearly no loss in the next 290 h of operation. XPS and XRD analyses, before the stability test, display the presence of copper oxide in the material. The compositional analyses of the anode and the cathode, before and after the life test, indicate an excessive loss of copper from the cathode. These physical characterizations and the life tests indicate that the enhanced activity of Pt-Cr-Cu/C material may be due to the combined effects of improved wetting of the catalyst particles by the Nafion solution (due to the presence of copper oxide) and of the Raney-type Pt-Cr-Cu alloy formation (due to the loss of nonnoble metal components).

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