

Improved Electrocatalytic Oxygen Reduction Performance of Platinum Ternary Alloy-Oxide in Solid-Polymer-Electrolyte Fuel Cells

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ABSTRACT

The effect of base metal oxide (noble metal oxide) in a Pt-Cr-Cu alloy catalyst is investigated for the oxygen reduction reaction in a solid-polymer-electrolyte fuel cell. The cathode mass activities at 0.9 V for Pt, Pt-Cr alloy, Pt-Cr-Cu alloy, and a mixture of Pt-Cr-Cu alloy with base metal oxide are compared. The enhancement factor is largest (about 6 times) for the mixture of Pt-Cr-Cu alloy with base metal oxide, compared to Pt-Cr and Pt-Cr-Cu alloys (about 2 times). The higher electrocatalytic activity of this material may be due to the combined effects of the Pt-Cr-Cu alloy and the base metal oxide. The physical and electrochemical characterizations are carried out using various techniques like x-ray diffraction, transmission electron microscopy, cyclic voltammetry, polarization, and ac impedance.

Research interest in the solid-polymer-electrolyte fuel cells (SPEFCs) is increasing due to the possible applications in electric vehicles. The commercial viability of H_2/O_2 SPEFCs depends on the effective utilization of platinum and the cost of production of the polymer membranes. The problems related to the effective utilization of platinum may be dealt with both by modifying electrode fabrication methods and by using more active platinum alloy electrocatalysts in the electrodes, especially in the cathodes. In the liquid electrolyte fuel cells, a three-dimensional (3D) reaction zone of catalyst-electrolyte-oxygen is easily attainable for increasing the platinum utilization efficiency. In SPEFCs, a modification of the electrode fabrication method is necessary because the solid electrolyte cannot creep into the gas-diffusion electrodes by surface tension to produce a 3D reaction zone. Recently, low platinum loaded electrodes in SPEFCs have been demonstrated with a 3D reaction zone by impregnating Nafion into the active layers of the gas-diffusion electrodes.¹⁻³ Further decrease in the platinum loading at the cathode may be obtained by employing more active alloy electrocatalysts instead of pure platinum.⁴

Since anions are chemically bound to the backbone of perfluorosulfonic acid membranes and the cell operation temperature is relatively low, the corrosion problems are minimized compared to other liquid acid electrolytes. It has been recommended that the nonprecious metals and their oxides can be evaluated as alternatives to the platinum catalysts, as they may be stable in polymeric electrolytes at relatively low temperatures, though they may lack stability in concentrated phosphoric acid.⁵ The mixed oxide catalysts of the binary and ternary alloys of noble metals and transition metals have been studied for the oxygen evolution reaction in solid polymer electrolyte water electrolyzers.⁶ The oxide pyrochlores of nonprecious metals are more active and stable in concentrated acid electrolytes like H_2SO_4 , if an interpenetrating solid polymer electrolyte is introduced between the acid electrolyte (liquid) and the electrode.⁷ Recently, binary, ternary, and quaternary platinum alloys with the base metals of Cu, Ni, and Co have been used as efficient and stable electrocatalysts in liquid acid electrolyte fuel cells.⁸ We have shown that Pt-Cr-Cu alloy is a better electrocatalyst than Pt and Pt-Cr alloy for the oxygen reduction reaction in liquid acid electrolytes.⁹

We present data here to show that an electrocatalyst (designated by Pt-Cr-Cu₆₀) containing both Pt-Cr-Cu alloy and a base metal oxide (noble metal oxide) has higher activity than Pt, Pt-Cr alloy, or Pt-Cr-Cu alloy in the cathode of SPEFCs below 80°C. We have carried out different microstructural characterizations such as x-ray dif-

fraction (XRD) and transmission electron microscopy (TEM) and electrochemical characterizations such as polarization, ac impedance, and cyclic voltammetry on a series of electrodes to obtain various physical, kinetic, conductivity, and performance parameters of the SPEFC systems.

Experimental

Platinum was deposited on pretreated carbon black using a platinum complex. The binary and ternary materials, viz. Pt-Cr and Pt-Cr-Cu, were prepared from platinum-on-carbon and the salts of base metals. The preparation of electrocatalysts, construction of a single-cell test station, and characterization techniques are explained briefly in this Section.

Preparation of electrocatalysts.—Pretreatment of carbon.—The loss of the electrocatalyst surface area, during the catalyst preparation process, and the prolonged use in the fuel cells, occurs due to the surface migration of the crystallites of the catalysts on the carbon support. This loss may be reduced by producing irregular channels on the surface of the support before loading the catalyst (metal). In the pretreatment procedure, the carbon support was subjected to a partial weight loss by a catalyzed oxidation using CuO to produce the channels on the surface. The catalytic oxidation of carbon support by copper oxide was carried out as follows:¹⁰ a mixture of carbon powder (30 g, Vulcan XC-72, Cabot Corp.) and cupric acetate solutions (0.3 g in 100 ml water) was thoroughly blended for 4 h and then dried in the air and vacuum ovens. Approximately 2 g of this dried powder was placed in a preweighed porcelain boat. The boat was then introduced into a tubular furnace and heated to 570°C in a flowing nitrogen atmosphere. This temperature was maintained for 15 min in the nitrogen atmosphere and for 3 min in the oxygen atmosphere. Then the boat was allowed to cool to room temperature in the nitrogen atmosphere. The weight of the powder was determined, and the boat was reintroduced into the furnace after stirring the powder. This procedure was repeated until a weight loss of approximately 30% was obtained. The powder was then washed with 50% nitric acid to remove copper. Then it was thoroughly washed with water to remove nitric acid traces. The powder was then dried in a vacuum oven at 110°C for 24 h. Finally, this carbon powder was sifted through a 100-mesh screen.

Preparation of platinum-on-carbon.—Dinitrodiammine-platinum(II) complex was prepared from the reaction between potassium hexachloroplatinate(IV), $NaNO_2$, and 30% aqueous ammonia. The preparation procedure for potassium hexachloroplatinate(IV) is reported elsewhere.¹¹ A mixture of the pretreated carbon and a known amount of this platinum complex dissolved in 50 weight percent (w/o)

* Electrochemical Society Student Member.

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nitric acid was heat-treated at 185°C for 12 h (ca. 10 w/o Pt/C). One part of this material was heat-treated at 900°C in a flowing nitrogen atmosphere for 1 h and cooled to room temperature. The powder thus obtained was sifted through a 100-mesh screen and used as the precursor for the preparation of binary and ternary electrocatalysts.

Preparation of Pt-Cr and Pt-Cr-Cu electrocatalysts.—1.5 g of platinum-on-carbon was dispersed in 80 ml of double-distilled water and ultrasonically blended for 15 min. The pH of the solution was adjusted to 8.0 by dropwise addition of dilute ammonium hydroxide, and the blending was continued during the entire preparation period. A solution of 0.302 g of ammonium chromate in 15 ml of double-distilled water was added to the mixture. The pH was then adjusted to 6.3 with dilute nitric acid, and the blending was continued for another 15 min. A solution of 1.288 g of copper nitrate in 15 ml of water was added to the mixture, and the blending continued for an additional 30 min, ensuring that the pH was maintained at 6.3. The suspension was then filtered, dried at 90°C for 12 h, allowed to cool to room temperature, and passed through a 100-mesh screen. The powder material thus obtained was divided into 3 portions. The first portion was heat-treated for 1 h at 900°C in a flowing nitrogen atmosphere to provide the Pt-Cr-Cu₆₀ electrocatalyst. The second portion was heat-treated at 185°C in air for 1 h to obtain an oxide mixture of the metals. The third portion of the powder was heated at 500°C in a flowing hydrogen atmosphere for 1 h to obtain a mixture of metals without alloying.

Another electrocatalyst designated as Pt-Cr-Cu₄₆ was prepared using the same procedure at 900°C under a flowing nitrogen atmosphere but with a lower content of copper using 0.485 g of copper nitrate. Pt-Cr alloy was prepared in the same way by excluding the addition of copper salt. The preparation procedure and the key physical properties of a Pt-Cr-Cu alloy designated by Pt-Cr-Cu₂₆ are reported elsewhere.⁹ The copper content in the Pt-Cr-Cu materials is in the following order: Pt-Cr-Cu₆₀ > Pt-Cr-Cu₄₆ > Pt-Cr-Cu₂₆. Here the numerals represent the actual weight percentage of copper in the Pt-Cr-Cu catalysts. Small portions (100 mg) of the electrocatalysts, namely, Pt-Cr-Cu₆₀ and Pt-Cr-Cu₄₆, were subjected to 15 or 360 min leaching in nitric acid at pH 3 to remove a part of the unalloyed copper and copper oxide.

Preparation of backing layers.—About 40 mg of pretreated carbon black was made into a paste from an aqueous suspension of Teflon (40% PTFE/C) and three drops of water. The paste was then applied on a stainless steel wire mesh (100 × 100, 3 cm²) and dried until small cracks appeared on the paste. It was then hot pressed at ca. 300°C between two highly polished brass plates for about 5 min at a pressure of 1000 bar. This thin carbon paper served as a backing layer in a gas-diffusion electrode.

Preparation of anode/membrane/cathode assembly.—Carbon-supported Pt was used as the anode in all the cells used here. Carbon-supported Pt, Pt-Cr, or Pt-Cr-Cu was used as the cathode electrocatalyst. A known amount of powder of each electrocatalyst was blended ultrasonically in 5 w/o Nafion solution (Aldrich) diluted in 0.3 ml water. The catalyst paint thus obtained was then brushed on the carbon backing layer with area 3 cm². The dry Nafion loading in all electrodes was maintained either at 6.6 or 2.6 mg/cm². The electrode was then allowed to dry for ca. 12 h under ambient conditions. It was dried further in a vacuum oven at 70°C for 1 h. A precleaned Nafion 117 membrane (Aldrich) was then pressed between the electrodes at 120°C and 60 atm pressure for 40 s to obtain a single-cell assembly.¹²

Construction of single-cell test fixture and single-cell test station.—A single-cell test fixture was made using two copper blocks provided with two cylindrical quartz-sheathed resistive heaters, thermocouples, gas-feed tubes, and gaskets. The copper blocks were pressed between two stainless steel end plates with Teflon sheet insulation as shown in Fig. 1. Two porous nickel disks placed on the

copper blocks (provided with perforated copper strips) were used as current collectors. The porous nickel disk was prepared as follows: 3 g of nickel powder sieved through 200-mesh screen was thoroughly mixed with 1.5 g of NH₄HCO₃ and made into a disk of 5 cm² area using a press at the pressure of 700 bar. The disk thus obtained was heated at 150°C in a flowing nitrogen atmosphere to remove NH₄HCO₃, and the temperature was raised to 850°C under hydrogen atmosphere. The heat-treatment was continued at this temperature for 30 min and followed by cooling to room temperature.

A single-cell test station, as shown in Fig. 1, was constructed to carry out the fuel-cell tests at different pressures of the reactant gases under controlled humidification conditions. A similar design has been reported elsewhere.¹³ The electrical insulation of the single-cell test fixture from the rest of the test station was maintained by using Teflon tubing between the test fixture and the humidifiers and the traps. The traps were introduced in the cell line to collect water, in case of condensation of the excessive water vapor or due to the back pressure. The polarization and impedance measurements were carried out using electrical probes connected to the copper blocks.

Physical and electrochemical characterizations.—Chemical analysis of the prepared materials was carried out with an atomic absorption spectrophotometer (Instrumentation Laboratory, Model 257) using the slurry-injection technique.¹⁴ A small portion (12 mg) of the electrocatalyst powder sieved through 100-mesh screen was heated at 80°C in 6 ml of concentrated HCl for 5 min. Then 2 ml of concentrated HNO₃ was added, and the heating was continued at 80°C for the next 10 min. The solution was then made up to 40 ml, and a few drops of Triton X-100 were added to the slurry to ensure uniform dispersion. About 0.15 g of LaCl₃ also was added to the slurry to minimize interference due to the presence of other metal ions. The slurry was finally made up to 50 ml, stirred, and aspirated into the flame. Aqueous standards of each element were run with the suspended carbon particles in the solutions.

For structural analysis, a Siemens KV IV x-ray diffractometer was used with Co-K_α radiation. The particle-size measurement was carried out using a Philips M300 TEM. Elemental composition found by the atomic absorption studies was cross-checked with a Kevex energy dispersive x-ray spectrometer (EDS) fit with a Hitachi 2300 scanning electron microscope (SEM). The conductivity measurement of Nafion 117 membrane was carried out under different wet conditions using a compartmented mercury cell shown in Fig. 2.¹⁵ The polarization studies were carried out on a 3-cm² single cell at 80°C with Pt anode (Pt loading = 0.44 mg/cm²) and Pt (Pt loading = 0.44 mg/cm²) or Pt-Cr (Pt loading = 0.44 mg/cm²) or Pt-Cr-Cu (Pt loading = 0.37 mg/cm²) cathode. Hydrogen and oxygen gas pressures were maintained at 4 and 5 atm, respectively. Cell potentials were corrected for iR losses by means of the current-interruption technique. Cyclic voltammetric studies were carried out at 50°C between 0.05 and 1.0 V vs. reversible hydrogen electrode (RHE) with a scan rate of 100 mV/s. Argon gas was maintained at the working-electrode compartment during this study. Cyclic voltammograms were recorded using Kipp & Zonen Model BD90 X-Y(t) recorder. The impedance studies of the systems were carried out using Princeton Applied Research (PAR) Model 388 electrochemical impedance software. The high frequency range of 5 to 100,000 Hz was controlled by a lock-in amplifier, and the low frequency range measurements below 5 Hz were made by utilizing a fast Fourier transform (FFT) approach. All the electrochemical measurements were carried out using a PAR 273 potentiostat.

Results and Discussion

Microanalysis of the electrocatalysts.—The elemental compositions determined by the atomic absorption technique deviate slightly from the EDS studies as shown in Table I. The compositions found from the atomic absorp-

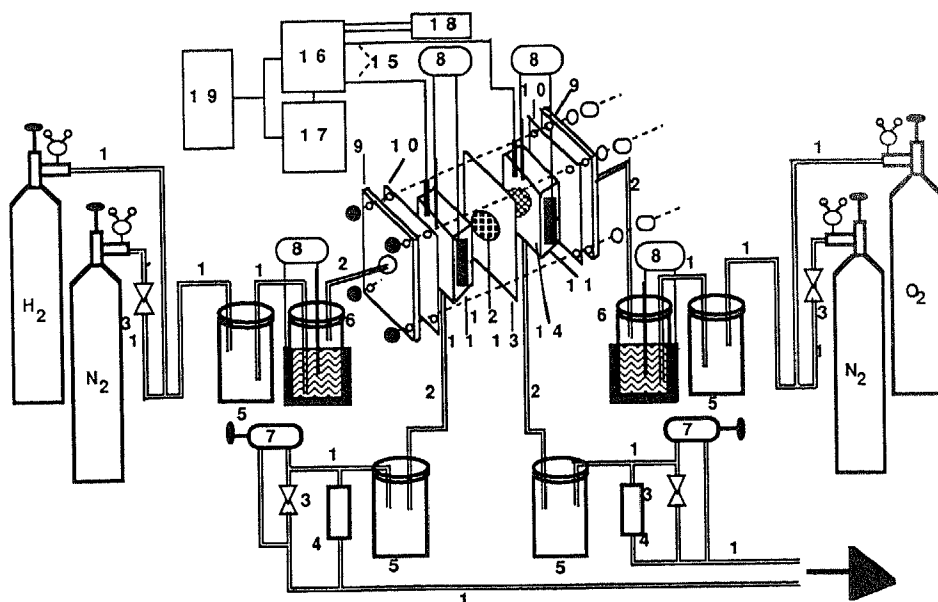


Fig. 1. Schematic diagram of single-cell test station.

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|---|------------------------------|
| 1 copper tubing | 12 electrode |
| 2 Teflon tubing | 13 membrane |
| 3 valves | 14 gasket |
| 4 flow meters | 15 current collecting probes |
| 5 stainless steel traps | 16 potentiostat |
| 6 humidifiers | 17 lock-in amplifier |
| 7 back pressure regulators | 18 recorder |
| 8 temperature controllers | 19 computer |
| 9 stainless steel end plates | |
| 10 Teflon insulators | |
| 11 copper blocks with gas feed tubes, heaters, thermocouples and current collectors | |

tion technique are used here as it is more reliable than the EDS method.

X-ray diffractograms of different electrocatalysts, along with pure platinum and pure copper, are shown in Fig. 3. All the electrocatalysts are showing the most prominent (111) diffraction peaks between the (111) peak of pure platinum ($d = 2.26 \text{ \AA}$) and the (111) peak of pure copper ($d = 2.09 \text{ \AA}$). The Pt-Cr electrocatalyst shows a decrease in lattice constant compared to Pt as is observed by the higher diffraction angle of the (111) peak compared to the (111) peak of Pt. The symmetric shape of diffraction peak profile of the (111) peak of Pt-Cr indicates the existence of a homogeneous single-phase alloy. Similar results are obtained for Pt-Cr-Cu₂₆. It is not known whether these alloys are intermetallic compounds or solid solutions. The shape of the

(111) peak profile of the electrocatalyst designated by Pt-Cr-Cu₆₀ is asymmetric and is close to the (111) peak of copper. This indicates the absence of single-phase homogeneous alloys and probably is due to the existence of both Pt-Cr-Cu alloy and copper. The additional peaks due to the presence of copper oxide are observed at $d = 2.31 \text{ \AA}$ and at $d = 2.53 \text{ \AA}$. On leaching in nitric acid for 15 or 360 min, there is a shift of the (111) peak position toward a low diffraction angle without developing any peak corresponding to pure Pt or Pt-Cr alloy. This study indicates the coexistence of Pt-Cr-Cu alloy along with the copper metal and the copper oxide. The compositional analysis after leaching for 360 min indicated more than 30 w/o copper loss from Pt-Cr-Cu₆₀, but XRD still indicated the presence of Cu and CuO. Hence the electrocatalyst Pt-Cr-Cu₆₀ may be represented tentatively, on the basis of weight, as Pt-Cr-Cu_{1-x}(CuO)_{x>0.3}. Similar observations are obtained for non-leached and leached Pt-Cr-Cu₄₆ electrocatalysts.

TEM micrographs of Pt, Pt-Cr, and Pt-Cr-Cu₆₀ are shown in Fig. 4. These show that for Pt and Pt-Cr electrocatalysts

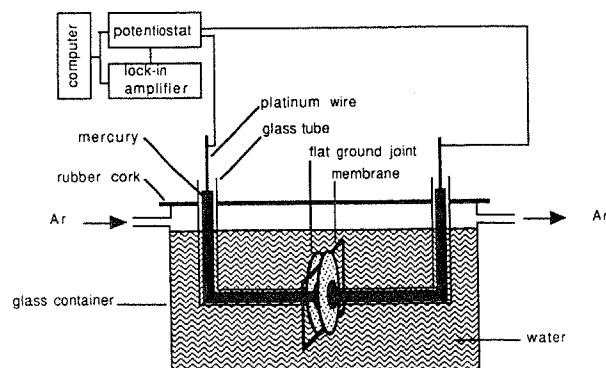


Fig. 2. Compartmented mercury cell for the measurement of conductivity of a polymer membrane under different wet and dry conditions.

Table I. Elemental composition of the electrocatalysts obtained from the atomic absorption studies.

Electrocatalyst	Composition (w/o)		
	Pt	Cr	Cu
Pt-Cr	88.60 (90.62)	11.40 (9.38)	
Pt-Cr-Cu ₂₆	57.05	17.05	25.90
Pt-Cr-Cu ₄₆	43.00	11.40	45.60
Pt-Cr-Cu ₆₀	25.50 (26.94)	14.10 (16.75)	60.40 (56.31)
Pt-Cr-Cu ₆₀ (L)	36.20	16.70	47.10

Composition found from the energy dispersive x-ray studies is shown in parenthesis; L indicates the form of the material leached in nitric acid for 15 min.

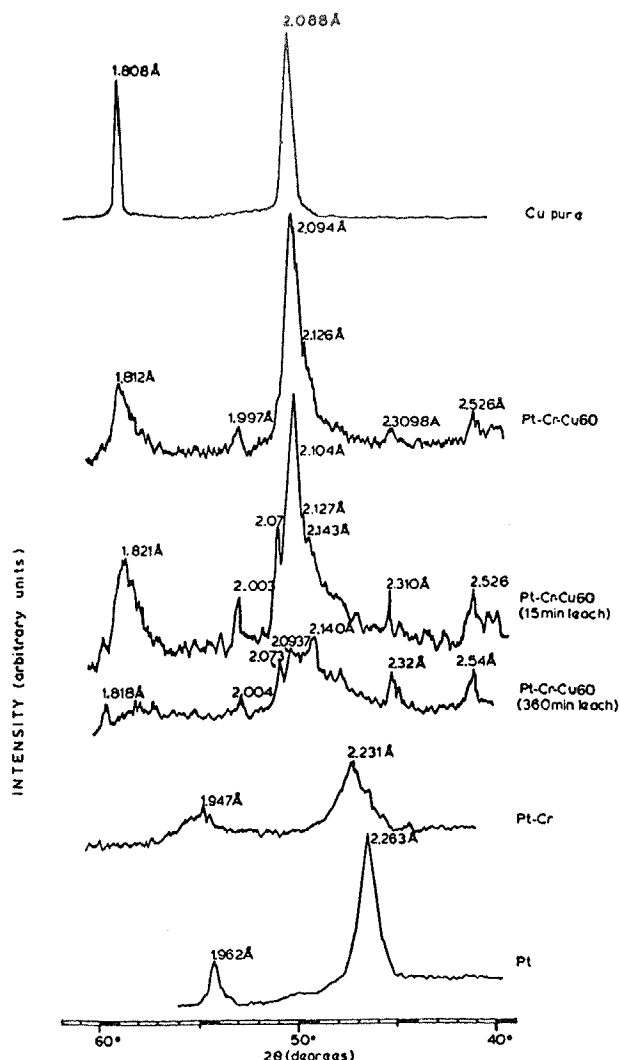


Fig. 3. X-ray diffractograms of different electrocatalysts.

there is a narrow range of particle-size distribution (22 to 98 Å) with a relatively uniform distribution of the particles over the carbon support. A broad particle size distribution (25 to 201 Å) is observed for Pt-Cr-Cu₆₀.

Conductivity of a polymer membrane.—The polymer membrane used in a single-cell assembly becomes dry due to the pressing of the membrane between the electrodes at 120°C. Hence, we must increase the conductivity of the membrane by increasing the water content before carrying out the performance evaluations of the electrocatalysts in the fuel cells. This is usually done by the humidification of hydrogen and oxygen gases after mounting the single cell in the test station.¹² To reduce the time of the on-line humidification process here, the single-cell assembly was first soaked in nanopure water at room temperature and then mounted in the test station.

The minimum water-soaking time of the membrane to achieve maximum conductivity at room temperature was determined from the ac impedance measurements using a compartmented mercury cell shown in Fig. 2. Initially, the impedance measurements were carried out in a flowing argon atmosphere without water in the glass container. The impedance spectra obtained after passing argon gas for 1260 and 2820 min are shown in Fig. 5. The appearance of the high frequency arc may be attributed to the heterogeneity of the polymer membrane under poor humidification conditions.¹⁶ The influence of this membrane relaxation process on the impedance spectrum disappears after introducing and maintaining water in the container for a mini-

imum period of 7 h, as shown in Fig. 5. This study thus indicates that a minimum soaking period of 7 h is necessary to attain maximum conductivity of the membrane. Therefore, the single cells tested here were soaked in water for about 7 h, blotted between Whatman filter papers to remove flowing water at the surface, and then mounted in the test station. The Nafion membranes used were pretreated in dilute hydrogen peroxide and nitric acid to remove organic and metal impurities, respectively. The appearance of a 45° line at low frequencies in all the impedance spectra shown in Fig. 5 may be due to the mass-transport influence of the trace impurities still present in the membrane.

Polarization studies.—These studies were carried out with Pt anodes and three different electrocatalysts, viz. Pt, Pt-Cr, and Pt-Cr-Cu, as cathodes. The performances of Pt and Pt-Cr-Cu cathodes under different Nafion loadings are shown in Fig. 6 and 7, respectively. Too much Nafion may impose mass-transport and impedance limitations, and too little may decrease catalyst utilization. Therefore, we must have an optimum amount of Nafion loading that provides sufficient contact with the catalyst particles. The mass-transport limitations were observed in all the polarization curves at higher current densities when the Nafion loading was 6.6 mg/cm². Such mass-transfer limitations were not observed, even at higher current densities, when the Nafion loading was 2.6 mg/cm² as shown in Fig. 6 and 7.

The cathode mass-activity polarization curves shown in Fig. 8 and the mass-activity values at 0.9 V shown in Table II demonstrate the superior electrocatalytic activity of Pt-Cr-Cu catalysts compared to Pt and Pt-Cr electrocatalysts. The Pt-Cr-Cu electrocatalysts obtained with a higher amount of copper, for example Pt-Cr-Cu₆₀, showed (Table II) nearly five times higher mass activity for 6.6 mg/cm² Nafion-loaded electrodes and more than six times higher mass activity for 2.6 mg/cm² Nafion-loaded electrodes compared to Pt electrodes.

Cyclic voltammetric studies indicated an increase in the electrochemically active area for Pt-Cr-Cu₆₀, compared to Pt and Pt-Cr alloy. The lower mass activity shown in Table II for the electrodes loaded with 6.6 mg/cm², compared to 2.6 mg/cm², may be attributed to the decrease of free catalyst sites for the oxygen reduction reaction. The decrease of free catalyst sites may be due to the increased adsorption of impurities on the catalyst sites from the thicker recast Nafion film. The effect of adsorption of impurities on the active catalyst sites is discussed further in the following Cyclic Voltammetry Section.

The Tafel slopes obtained at low overpotentials (between open-circuit potential and 0.82 V) for different electrocatalysts used here were in a narrow range between 79 and 88 mV/decade as shown in Table II. The impedance studies (discussed later) indicated no influence of a mass-transfer limitation under polarization up to 0.75 V for the electrodes loaded with 2.6 mg/cm² Nafion. If there were an influence of a diffusion limitation on the Tafel slope, there should have been an increase in the Tafel slope for 6.6 mg/cm² Nafion-loaded electrodes compared to 2.6 mg/cm² Nafion electrodes. Since nearly the same Tafel slope was obtained irrespective of Nafion loadings, we may suggest that the Tafel slope is not influenced by the mass-transport limitation at the low overpotential region. The experimentally obtained potential values (E_o) at 1 mA/cm² (very low polarization), Tafel slope (b), and the exchange current density (i_o) can be related by¹²

$$E = E_o - b \log(i) - R_i$$

where $E_o = E_r + b \log(i_o)$, i is the current density, R_i is the internal resistance of the cell, and E_r is the reversible potential. Higher E_o values and nearly the same Tafel slope of Pt-Cr-Cu₆₀ compared to Pt and Pt-Cr were obtained as shown in Table II. This indicates that the superior electrocatalytic activity of this material is displayed in the form of an increased exchange-current density. Relatively higher Tafel slopes of all the electrodes used here may be due to relatively larger crystallites of the electrocatalysts.¹⁷

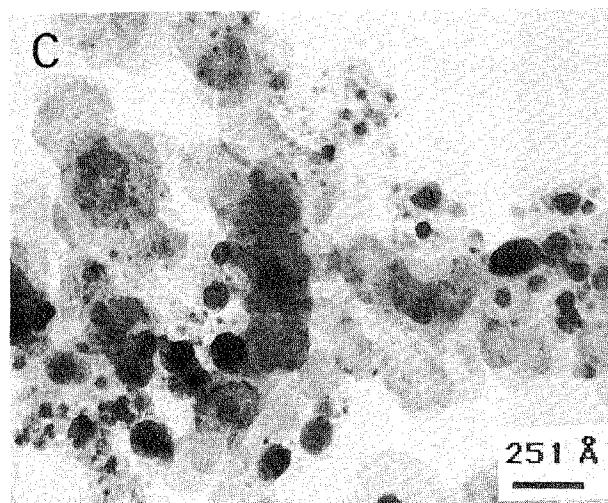
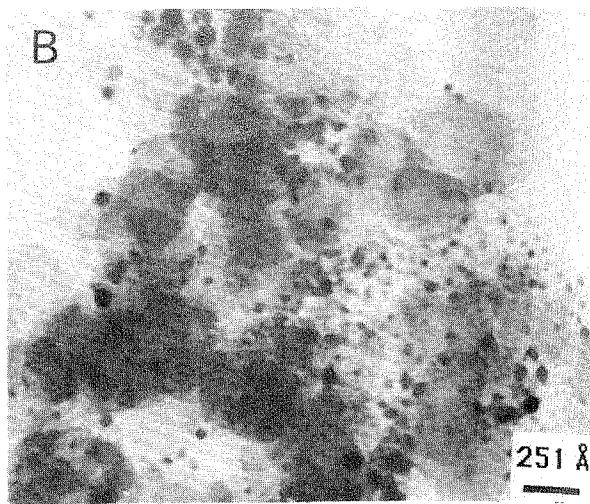
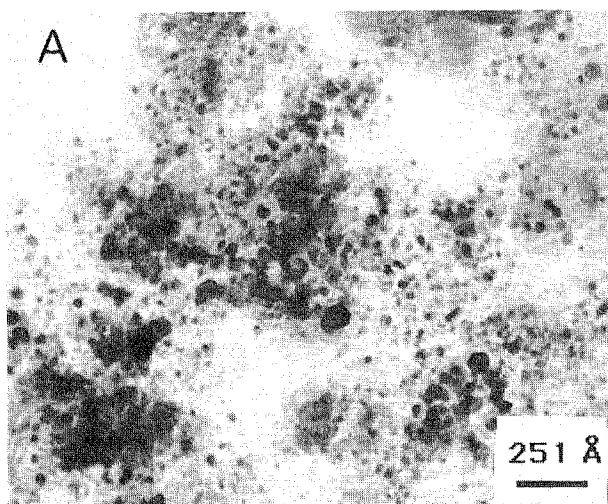


Fig. 4. TEM of (A) Pt, (B) Pt-Cr, and (C) Pt-Cr-Cu₆₀ electrocatalysts on Vulcan XC-72 carbon.

Generally, the enhanced electrocatalytic activities of Pt-alloys are attributed to various reasons like the decrease of nearest neighbor distance of platinum,¹⁸ the formation of Raney type platinum,¹⁹ and the coexistence of base metal oxides along with Pt or Pt-alloy crystallites.²⁰ XRD studies indicated a decrease in the nearest neighbor distance of platinum atoms in the alloys of Pt-Cr and Pt-Cr-Cu₂₆ compared to pure Pt. The diffraction peaks corresponding to the base metal or the base metal oxide were not detected in the XRD of these two materials. Thus, the higher mass activity (ca. two times) of these alloys at 0.9 V may be at-

tributed either to the improved dual-site adsorption mechanism (due to the decrease of nearest neighbor distance of platinum) or to the Raney type platinum formation (due to the loss of less noble components). In view of the fuel-cell operating conditions and the unstable nature of the less noble metals involved, the probable reason for higher activity of these alloys is the formation of Raney type platinum (surface roughening).

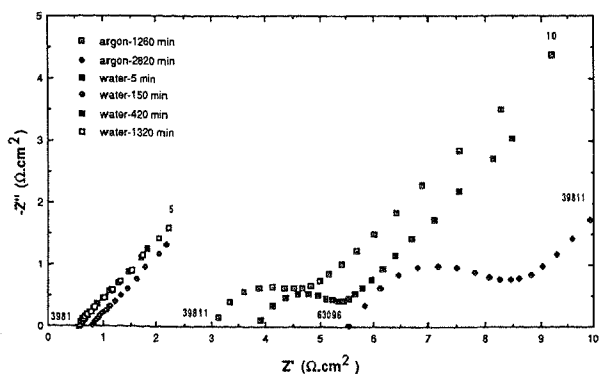


Fig. 5. Impedance spectra of the Hg/Nafion interface under different wetting conditions at room temperature. (The numbers indicate the frequency in hertz).

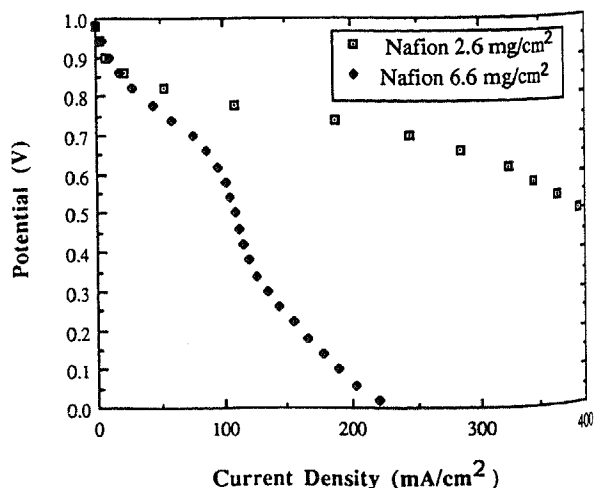


Fig. 6. Effect of different amounts of Nafion loading on the polarization curves of the Pt electrodes. (Pt loading was 0.44 mg/cm².)

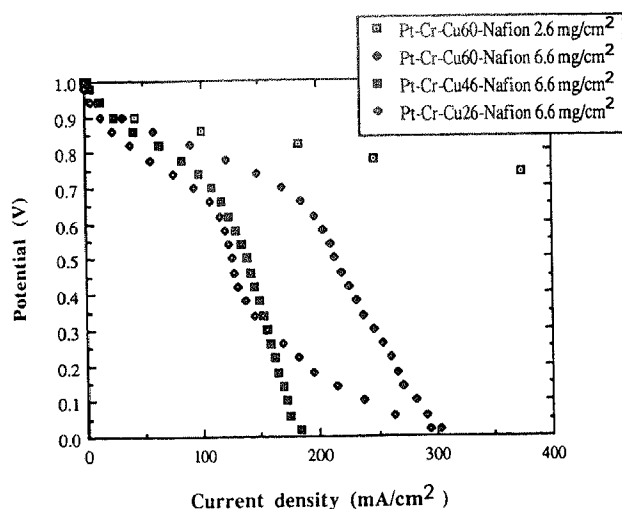


Fig. 7. Effect of different amounts of copper in the ternary electrocatalysts on the polarization curves. The effect of a different amount of Nafion loading on the polarization curves also is shown. (Pt loading was 0.37 mg/cm².)

In the higher copper-loaded Pt-Cr-Cu₄₆ and Pt-Cr-Cu₆₀ catalysts, the presence of copper metal and copper oxide was detected in the XRD studies. Thus the enhanced electrocatalytic activity of Pt-Cr-Cu₄₆ and Pt-Cr-Cu₆₀ (ca. six times), may be due to the coexistence of base metal oxide along with Pt-Cr-Cu alloy. The enhancement effect of base metal oxide may not be truly catalytic. Although the exact role of the oxide promoter is not known, the enhanced activity of Pt-Cr-Cu alloy, due to the presence of base metal oxide, may be attributed to the improved spreading wetting and/or to the formation of Raney type Pt-Cr-Cu alloy (dissolution of base metal and base metal oxide).

Spreading wetting can be explained as a phenomenon in which the first fluid (a liquid) spreads to displace the second fluid (usually air) which is already in contact with the solid. This spreading process increases the interfacial area between the solid and the liquid. In the preparation of anode/membrane/cathode assembly section, the catalyst paint was prepared from a mixture containing the catalyst powder (solid) and the dilute Nafion solution (liquid). Hence, we may suggest that the base metal oxide can act as a flux and help the wetting of the active electrocatalyst particles.²⁰ The presence of oxygen-containing compounds on the carbon support helps the impregnation of dissolved solid polymer electrolytes.³ On leaching the Pt-Cr-Cu₄₆ and Pt-Cr-Cu₆₀ catalysts in nitric acid for 15 min, a decrease in

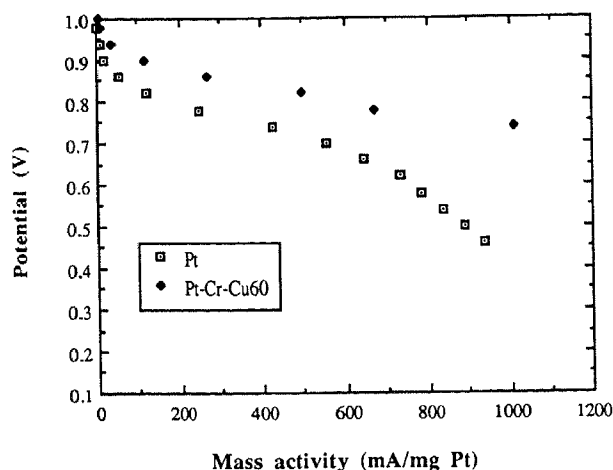


Fig. 8. Cathode-mass-activity comparison of the Pt and Pt-Cr-Cu₆₀ electrodes at 80°C, according to the polarization curves of Fig. 6 and 7. (Nafion loading was 2.6 mg/cm².)

Table II. Mass activity and different kinetic parameters under different Nafion loadings.

Electrocatalyst	Nafion loading (mg/cm²)	Mass activity at 0.9 V (mA/mg Pt)	Kinetic parameters	
			E _o (V)	Tafel slope (mV/decade)
Pt	6.6	18.4	0.970	87
Pt	2.6	18.6	0.974	83
Pt-Cr	6.6	38.0	0.991	79
Pt-Cr-Cu ₂₆	6.6	42.4	1.000	88
Pt-Cr-Cu ₄₆	6.6	66.8	0.998	87
Pt-Cr-Cu ₆₀	6.6	87.9	1.020	85
Pt-Cr-Cu ₆₀	2.6	116.8	1.017	85
Pt-Cr-Cu ₆₀ (L)	6.6	48.4	1.000	83

L indicates the form of the material leached in nitric acid for 15 min.

electrocatalytic activity was observed as shown in Fig. 9 and Table II. The decrease of activity for these leached catalysts may be attributed to the less effective wetting of the catalyst particles by Nafion solution because of the partial loss of copper oxide. After leaching, the XRD pattern showed a shift of (111) peak toward a lower diffraction angle (Fig. 3). Since the XRD pattern did not show any peak corresponding to pure Pt and Pt-Cr alloy after leaching, the catalyst may be a Pt-Cr-Cu alloy with less copper content in it (Raney type Pt-Cr-Cu alloy). If the enhancement effect was due only to Raney type Pt-Cr-Cu alloy formation, a decreased activity due to acid leaching may not be expected. Thus, the enhanced activity of Pt-Cr-Cu₆₀ and Pt-Cr-Cu₄₆ may be related to the combined effects of Raney type Pt-Cr-Cu alloy formation and the base metal oxide.

The enhanced electrocatalytic activity of Pt-Cr-Cu₆₀ or Pt-Cr-Cu₄₆ may be due to the mixture of metals or mixture of oxides of the metals without any portion of alloy of Pt-Cr-Cu, although this is improbable as these catalysts were prepared at a high temperature (900°C). However, this possibility was verified as follows: a mixture of metals-on-carbon, prepared at 500°C in a flowing hydrogen atmosphere, was tested by polarization studies as shown in Fig. 10. It showed only 11 mA/mg Pt cathode mass activity at 0.9 V. Similar studies were carried out with a mixture of oxides of the metals-on-carbon prepared at 185°C in air (Fig. 10). The open-circuit potential was only ca. 0.85 V. Thus the improved electrocatalytic activity of Pt-Cr-Cu₆₀ or Pt-Cr-Cu₄₆ may be interpreted in terms of the combined effects of the spreading wetting of the active catalyst particles by Nafion solution (due to the presence of oxide promoters) and of the Raney type alloy formation (due to the loss of less noble metal and metal oxide).

Cyclic voltammetry.—Hydrogen desorption peaks of the cyclic voltammograms (Fig. 11) indicate the higher electro-

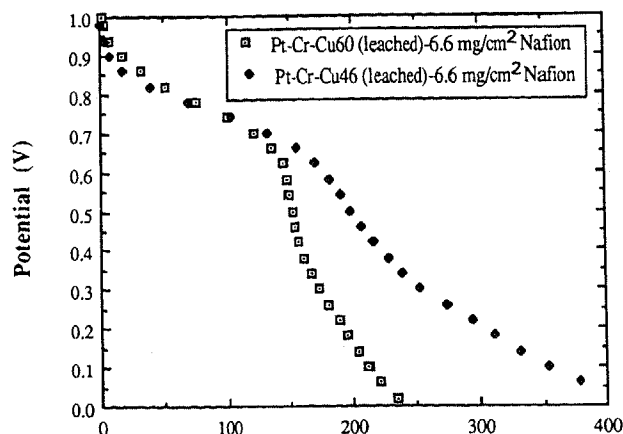


Fig. 9. Polarization curves of the Pt-Cr-Cu₄₆ and Pt-Cr-Cu₆₀ electrodes after leaching in nitric acid at pH 3 for 15 min. (Pt loading was 0.37 mg/cm².)

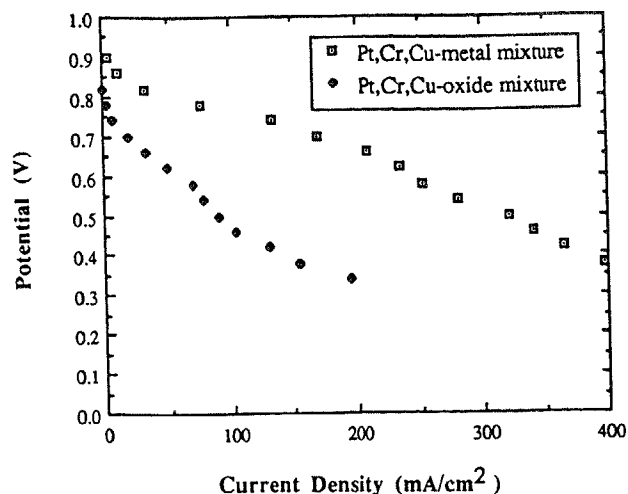


Fig. 10. Polarization curves for the metal mixture of Pt, Cr, and Cu and the oxide mixture of Pt, Cr, and Cu. (Pt loading was 0.37 mg/cm^2 , and Nafion loading was 2.6 mg/cm^2 .)

chemically active surface area for Pt-Cr-Cu₆₀ compared to Pt and Pt-Cr, although the particle size of Pt-Cr-Cu₆₀ is much larger than Pt or Pt-Cr. This may be attributed to spreading wetting of the active alloy electrocatalyst particles due to the presence of oxide promoters. The adsorbed trace impurities on the active catalyst sites interfere with the electrode reactions.²¹ Uribe *et al.* recently have carried out cyclic voltammetry studies in dilute sulfuric acid on bare platinum microelectrodes and on recast Nafion-coated platinum microelectrodes.²² Similar studies have been carried out by Gottesfeld *et al.* on rotating disk electrodes.²³ These studies indicated a loss of the electrochemically active surface area for the recast Nafion-coated electrodes compared to the bare electrodes (due to the adsorption of the organic impurities originating from the recast Nafion films). Thus the lower coulombic charge for the hy-

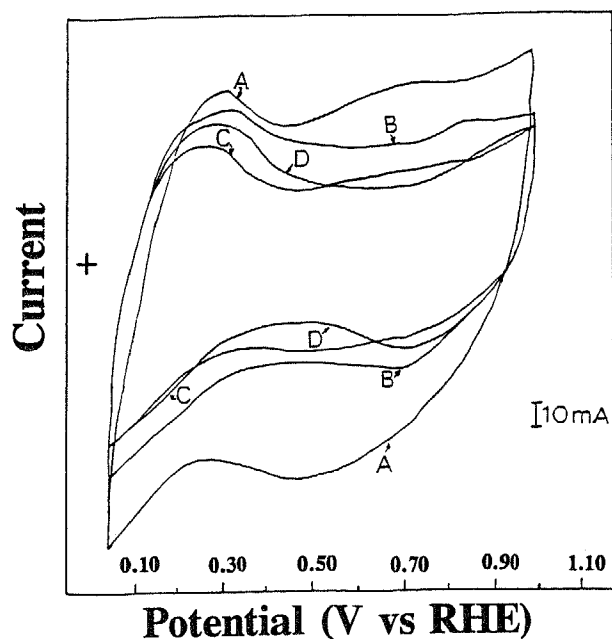


Fig. 11. Cyclic voltammograms of (A) the carbon-supported Pt, (B) Pt-Cr, and (C and D) Pt-Cr-Cu₆₀ electrodes at 50°C under argon atmosphere. Nafion loading was 6.6 mg/cm^2 in all electrodes except D in which it was 2.6 mg/cm^2 . Platinum loadings for the Pt, Pt-Cr, and Pt-Cr-Cu₆₀ electrodes were 0.44 mg/cm^2 , 0.44 mg/cm^2 , and 0.37 mg/cm^2 , respectively. The geometric electrode area was 3 cm^2 , and the scan rate was 100 mV/s .

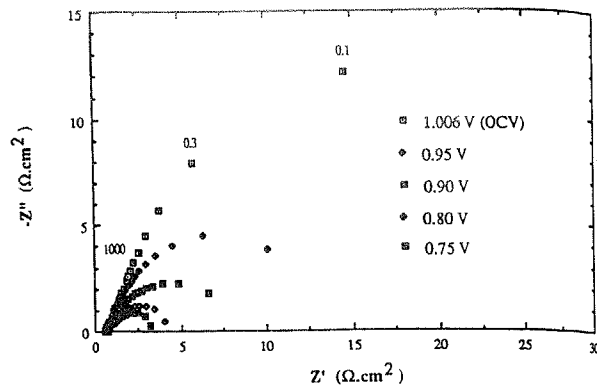


Fig. 12. Complex-plane plots of the Pt-Cr-Cu₆₀/Nafion interface at different potentials for the oxygen reduction reaction at 80°C . (Nafion loading was 2.6 mg/cm^2 , and the numbers over the spectra indicate frequency in hertz.)

drogen desorption peak of Pt-Cr-Cu₆₀ for 6.6 mg/cm^2 Nafion loading compared to 2.6 mg/cm^2 Nafion loading may be attributed to increased blockage of catalytic sites by organic impurities originating from the thicker recast Nafion film.

AC impedance measurements.—The impedance spectra obtained for Pt-Cr-Cu₆₀/Nafion interface at different potentials are shown in Fig. 12. Nafion loading in this electrode was 2.6 mg/cm^2 . The observed high-frequency resistance (ca. $0.5 \Omega \cdot \text{cm}^2$) indicated the necessity for improvement in single-cell fabrication methods to decrease contact resistance between the membrane and the electrodes. As expected, the diameter of the arc in Fig. 12 decreases as the overpotential is increased due to a decrease in the faradaic resistance.^{16,24} The absence of any high frequency loop at all potentials indicated a good humidification of the membrane. The influence of a mass-transport limitation was not observed in the impedance spectra (no 45° line in the Nyquist plot) even at 0.75 V . Thus the cathode mass-activity values obtained at 0.9 V and the Tafel slopes obtained above 0.82 V for 2.6 mg/cm^2 Nafion-loaded electrodes may be considered free of mass-transport limitations.

Stability test.—This test was carried out for a short term for the Pt-Cr-Cu₆₀ cathode at 100 mA/cm^2 and 50°C . There was about a 9-mV performance loss observed from the initial potential of 782 mV in the first 10 h period of operation. In the next 20 h of operation, no voltage drop was observed. The performance loss in the initial stage of cell operation may be due to conditioning of electrode/electrolyte interface or due to instability of the electrode because of the presence of the base metal oxide. The oxides of nonprecious metals may be made stable even in concentrated acids like H_2SO_4 if an interpenetrating solid polymer electrolyte is used.⁷ Appleby and Yeager have suggested that the oxides of nonprecious metals can be tried as alternatives to the Pt catalysts, as they may be stable in polymer electrolyte, although they may lack stability in the liquid acid electrolytes.³ A relatively long-term stability test at the current density of 200 mA/cm^2 is in progress.

Conclusion

The XRD and the acid-leaching studies indicated the presence of copper oxide along with Pt-Cr-Cu alloy in Pt-Cr-Cu₆₀ (higher copper loaded electrocatalyst) prepared at 900°C . The cyclic voltammetry studies showed an improved electrochemically active area for Pt-Cr-Cu₆₀ electrodes, compared to Pt or Pt-Cr alloy electrode. The comparison of the cathode mass activity at 0.9 V between Pt, Pt-Cr alloy, and Pt-Cr-Cu alloy, indicated about two times higher activity for the alloys than Pt. The mixture of Pt-Cr-Cu alloy with base metal oxide (Pt-Cr-Cu₆₀) showed about 6 times higher mass activity than Pt. The exact role of the base metal oxide is not clear. The enhanced activity of this elec-

trocatalyst may be due to the combined effects of the Raney type Pt-Cr-Cu alloy and of the base metal oxide. A short-term stability test indicated nearly stable performance for 20 h after little loss of performance in the first 10 h of cell operation.

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Study of the Mechanism of the Hydrogen Evolution Reaction at Raney Nickel Electrodes in the Presence of Organic Compounds

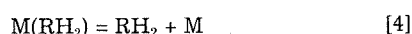
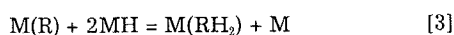
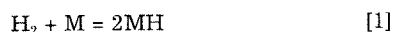
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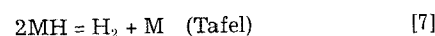
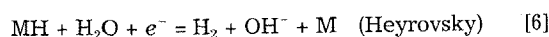
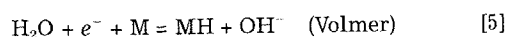
ABSTRACT

The hydrogen evolution reaction (HER) has been studied at Raney nickel electrodes in the absence and presence of several organic compounds. A poisoning effect of nonreducible organic substrates on the kinetics of the HER was studied. It was found that only pyridine had a strong inhibiting effect on the HER. A compound having one reducible double bond, *trans*-cinnamic acid, was used as a model in a study of the mechanism of the electrocatalytic hydrogenation (ECH) reaction and its influence on the HER. It was established that the HER proceeds via the Volmer-Heyrovsky reaction mechanism, and the slowest step is the Heyrovsky reaction.

The hydrogen evolution reaction (HER) is one of the most often studied cathodic reactions.¹⁻³ Indeed, hydrogen has lately been recognized as a valuable fuel which may well replace oil as an energy source. Hydrogen has also played a major role in synthetic organic chemistry in the well-known catalytic hydrogenation process by which an unsaturated compound, R, adsorbed at the surface of a catalyst M is reduced by the adsorbed hydrogen MH (reactions 1-4)⁴



Such reactions generally require high temperatures and pressures. Another method of reducing these compounds under much milder conditions is electrocatalytic hydrogenation (ECH), by which the adsorbed hydrogen is formed by electrolysis of water (reaction 5). The hydrogenation reaction is in competition with the hydrogen evolution (reactions 6 and 7 resulting from the electrochemical or chemical desorption of hydrogen



The efficiency of ECH is determined by this competition and depends on several factors: the relative rate constants of reactions 6 and 7 and 2 through 4, the substrate itself, its

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