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Pt Submonolayers on Ru Nanoparticles

A Novel Low Pt Loading, High CO Tolerance Fuel Cell Electrocatalyst

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A new method for the preparation of Pt-Ru and similar bimetallic electrocatalysts is reported. It involves a spontaneous deposition of Pt submonolayers on metallic Ru nanoparticles, which yields electrocatalysts with a considerably lower Pt loading and higher CO tolerance than the commercial Pt-Ru alloy electrocatalysts. The method offers a unique possibility to place the Pt atoms onto the surface of Ru nanoparticles, which very likely makes almost all of them available for hydrogen oxidation, in contrast to the Pt-Ru alloy catalysts that have Pt throughout the nanoparticles. Thus, an ultimate reduction of Pt loading can be achieved. It also facilitates a fine-tuning of the electrocatalyst's activity and selectivity by changing the coverage (the cluster size) of Pt for optimal performance under required CO tolerance levels.

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A great deal of effort has been devoted over the years to the development of platinum-ruthenium alloy electrocatalysts for the oxidation of methanol in fuel cells. More recent efforts have focused on improving the so-called CO tolerance of these catalysts, *i.e.*, their activity in the oxidation of hydrogen that is obtained by reforming methanol, which inevitably contains a certain concentration of carbon monoxide.[1] Despite considerable advances in the development of these electrocatalysts, their activity and CO tolerance are still unsatisfactory. This issue is one of the two major obstacles for a large-scale application of the polymer electrolyte membrane fuel cell (PEMFC), which seems to be the most promising energy system for electric vehicles and for on-site power generation. The second obstacle is the price of platinum whose loading is too high even in the best available electrocatalysts.

In this article we describe a new approach for obtaining electrocatalysts that can alleviate both above impediments. The new method is based on spontaneous deposition of Pt on Ru that we recently demonstrated for Pt [2] and Pd [3] deposition on a Ru(0001) single crystal surface, which involves a reduction of H_2PtCl_6 coupled with the oxide formation on Ru.[2] A selective Pt deposition on Ru (no deposition on carbon) is attainable without the application of an external potential.[4]

The preparation of bimetallic catalysts by surface modification of metal substrates has attracted considerable attention in catalysis[5] and electrocatalysis.[6] Most studies involve alloy formation and modifications of Pt surfaces, which include underpotential deposition (UPD) of metal adlayers, the so-called spontaneous or irreversible adsorption of nonnoble metal cations,[7,8] and spontaneous deposition of noble metals adlayers. The latter type of modification requires a subsequent application of potential and yields small coverages, as recently shown by Wieckowski and co-workers[9,10] for the deposition of Ru adlayers on Pt(111) and Pt(100) surfaces. The present deposition method can produce monolayer-to-multilayer coverages, of Pt [2] and Pd on Ru single crystals. If extended to Ru nanoparticles, it would open up an important possibility for tailoring Pt-Ru catalysts with an atomic level control.

The Pt-Ru bimetallic alloys are the best available electrocatalysts for the oxidations of reformate hydrogen.[11] It is generally believed that those catalysts operate through a bifunctional mechanism,[12] although the electronic effects cannot be ignored.[13,14] Spontaneous deposition of Pt on Ru nanoparticles can be used to control the Pt cluster size and to tune the electronic and catalytic properties of Pt-Ru catalysts. In addition, this approach facilitates a considerable reduction of Pt loadings by depositing Pt at the surface of Ru nanoparticles rather than having Pt throughout the Pt-Ru nanoparticles. In this paper, the results from scanning tunneling microscopy (STM) measurements of Pt deposition on Ru(0001), thin-film (Pt on carbon supported Ru) rotating disk electrode data, and subtractively normalized interfacial Fourier transform infrared (SNIFTIR) spectroscopy of CO adsorbed on Pt submonolayer on Ru(0001) are presented.

Experimental

The Ru(0001) single crystal 8 × 3 mm disk, obtained from Metal Crystals and Oxides, Cambridge, England, was additionally oriented to better than 0.1° and polished with diamond paste down to 0.3 μm. The surface preparation was carried out in an ultrahigh vacuum (UHV), following the standard procedure for Ru.[15] It consisted of two cycles of argon ion sputtering at room temperature and annealing at 1400°C, followed by five cycles of oxygen adsorption and desorption in an oxygen atmosphere of 10^{-7} Torr at 500 and 1400°C, respectively. The final flash annealing was done in UHV at 1400°C to remove the residual oxygen from the surface. The crystal was allowed to cool down in the vacuum chamber. The chamber was then filled with ultrapure Ar and the crystal was transferred from the UHV chamber into an Ar-filled glove box and immersed in the deoxygenated H_2PtCl_6 solution for a certain time. After the emersion from the solution, the crystal was thoroughly rinsed with 0.1 M H_2SO_4 and ultrapure water, and protected by a water drop, was transferred to an electrochemical or STM cell.

Ru nanoparticles dispersed on XC-72 active carbon (10% Ru on C), obtained from E-TEK, were reduced in H_2 atmosphere at ~300°C for 2 h. They were brought in contact with a deoxygenated solution of H_2PtCl_6 in 0.1 M $HClO_4$, containing a desired amount of Pt, after being cooled down to room temperature. Spontaneous deposition took place within 30-60 min in either H_2 or N_2 atmosphere. The catalyst was then dispersed in water to obtain dispersion necessary for the desired metal loading. The preparation of the thin-film rotating electrode was similar to the one described in literature.[16] Uniform catalyst dispersion was obtained by sonication and 10-20 μL was transferred onto a glassy carbon rotating electrode (5 mm in diam). After water evaporation, the catalyst was covered by a dilute Nafion solution, which after solvent evaporation left a film with thicknesses ranging from 0.001 to 0.1 μm. The E-TEK 20 wt % Pt:Ru on Vulcan XC 72 carbon catalyst, used for comparison of catalyst activity, was treated in a similar way.

Solutions were prepared from Optima* sulfuric acid obtained from Fisher and Milli-Q UV-plus water (Millipore). An Ag/AgCl/KCl (3M) electrode was used as a reference electrode and all potentials are quoted with respect to its standard potential. The *in situ* STM studies were performed using a Molecular Imaging Pico STM with a 300S scanner and a Molecular Imaging model 300S pico

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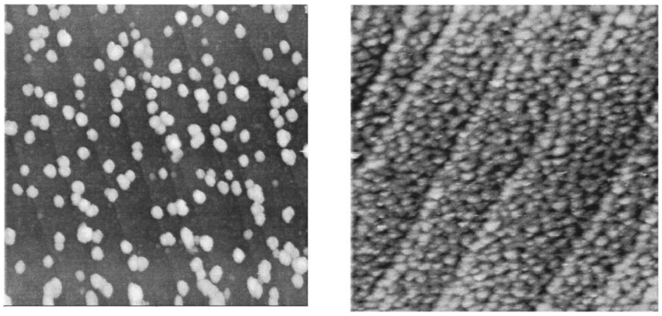

Figure 1. STM images (200 × 200 nm, left, and 100 × 100 nm, right) of spontaneously deposited Pt on Ru(0001) from solutions containing 0.1 and 10 mM H_2PtCl_6 in 0.1 M H_2SO_4, respectively. Images recorded at open circuit potentials with Z ranges of 5 (left) and 2 nm (right).

bipotentiostat. The cell, made of Teflon, exposed an area of *ca.* 0.3 cm^2 and had a volume of *ca.* 1.5 cm^3. Prior to each experiment, an STM tip was prepared by etching a 80:20 Pt + Ir wire in a $CaCl_2$ solution and insulating it with Apiezon wax.

The cell for *in situ* infrared spectroelectrochemical measurements and the optical path were described previously.[17] A Mattson RS-10000 spectrometer and a PAR 273 potentiostat were computer controlled using a program designed to set the potential of the working electrode alternatively to the sample or the reference potential for the working electrode prior to sample acquisition. The reference potential was constant and chosen to be just positive to the onset of hydrogen evolution in the corresponding electrolyte. 4096 scans were coadded in cycles of 128 scans each. 8 cm^{-1} resolution was used throughout the study. The SNIFTIR spectra, $-\Delta R/R$, are given in the figures, with the positive-going bands representing a gain of a particular species at the sample potential relative to that at the reference.

Results and Discussion

First, we illustrate the spontaneous deposition of Pt on a Ru(0001) single crystal by *in situ* scanning tunneling microscopy. The immersion of a UHV-prepared Ru single crystal in a solution containing platinum ions results in a formation of Pt deposits whose coverage and morphology depend on the platinum ion concentration of and the time of immersion. Unlike for the previously reported spontaneous deposition of noble metals on noble metals,[9,10] a multilayer Pt deposit can be obtained. Figure 1a shows the morphologies of two Pt deposits on a well ordered Ru(0001) surface. The Pt deposit obtained from a 0.1 mM H_2PtCl_6 + 0.1 M H_2SO_4 solution for a 2 min immersion consists of a large number of Pt clusters which have a columnar shape and a relatively uniform size. Their height is in the range of 3 to 5 nm (10-15 ML) and their diameter is between 6 and 10 nm (Fig. 2). The total amount of Pt deposited is between 4 and 5 ML. The Pt deposit obtained from the 10 mM H_2PtCl_6 in 0.1 M H_2SO_4 solution during 1 min deposition is shown in Fig. 1b. The entire Ru surface is covered with 2-6 nm-sized clusters with an average height of 2 ML. About 92% of the Ru surface is covered and the total amount of deposited Pt is approximately ~2 ML. The surface oxidation of Ru supplies the electrons for the reduction of Pt ions.[2]

Spontaneous deposition of Pt on carbon-supported Ru nanoparticles was found to occur after the sample was reduced in H_2 atmosphere at ~300°C for 2 h. This temperature is much lower than that required for bulk Ru preparation, which can be explained by the particle size effect. After cooling down to room temperature, the amount of 1 mM H_2PtCl_6 solution necessary to make the catalysts with the Pt:Ru ratio ranging from 1:20 to 1:5 was brought into contact with a sample. It is assumed that under H_2 or N_2 atmosphere all the Pt ions are deposited on Ru nanoparticles within 30-60 min. According to E-TEK, the average particle diameters for the Ru/C and Pt:Ru/C were 2 and 2-2.5 nm, respectively. After Pt deposition, the mean diam of the Pt-Ru nanoparticles was about 2.5 nm according to our transmission electron microscopy (TEM) measurements. The ratio of surface atoms to total atoms is roughly 0.45 for the 2.5 nm particles,[18] and for the 1:20 Pt:Ru sample the Pt coverage will be 1/9 (since $1/9 = 1/(20 \times 0.45)$. For the 1:5 Pt:Ru sample, the Pt coverage will be about 1/2. The catalytic activity of these electrocatalysts was determined by using a thin-film rotating disk electrode method as described below.

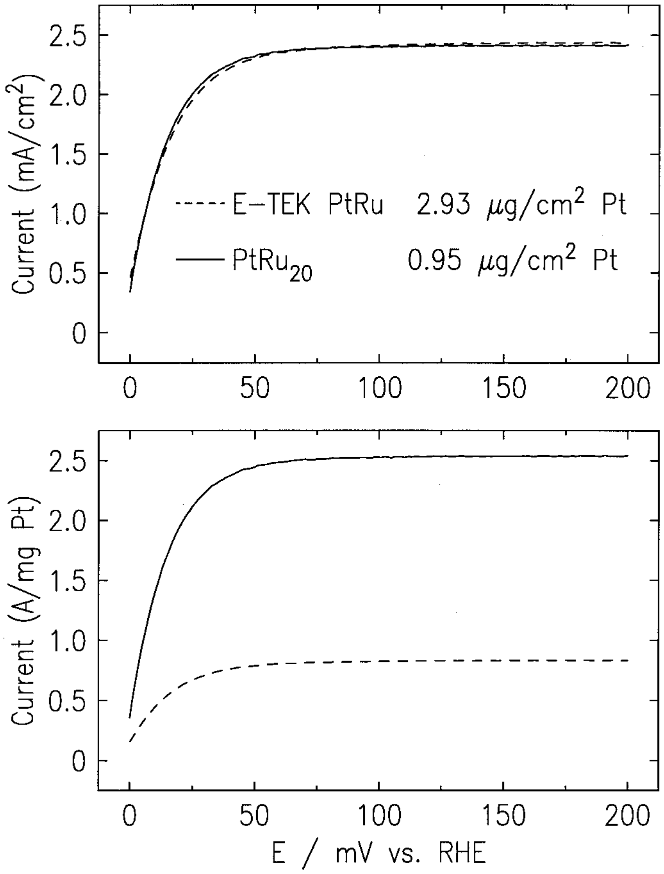

Figure 2. Polarization curves for the catalyst prepared by spontaneous deposition of Pt on Ru nanoparticles on Vulcan XC72 (solid line) and E-TEK's 20% 1:1 PtRu catalyst (dashed line) for the oxidation of H_2 in 0.5 M H_2SO_4 at 25°C obtained by using a thin-film rotating electrode at 2500 rpm (upper panel). Mass-specific activity of the above two electrocatalysts obtained from the data in the upper panel (lower panel).

Figure 2 displays a comparison of the activity of the PtRu 1:20 electrocatalyst prepared by spontaneous deposition of Pt on Ru, and E-TEK's PtRu 1:1 alloy electrocatalyst for the oxidation of H_2 in 0.5 M H_2SO_4. The polarization curves were obtained by using a rotating disk electrode (RDE) at 2500 revolutions per minute (rpm). The curves in the upper panel are nearly identical, although the Pt loading differs by a factor of three. Therefore, as shown in the lower panel, the mass-specific activity with respect to Pt for the catalyst obtained by spontaneous deposition of Pt is three times that of the E-TEK PtRu alloy. These results were obtained with very low Pt loadings and a very thin Nafion film (<0.01 um) in order to maximize the catalyst utilization and minimize the film diffusion resistance.

The mass-specific currents for H_2 oxidation were measured as a function of both the Pt loading and the Nafion film thickness by decreasing them gradually from the commonly used values.[16,19] For each sample, the current density at 50 mV was measured at 2500 rpm and normalized by the Pt loading. Although there are certain statistical errors resulting mainly from loading measurement and

Table I. Mass-specific current (J) measured at 50 mV at 2500 rpm for H_2 oxidation in 0.5 M H_2SO_4 at 25°C as a function of Pt loading and Nafion film thickness for the E-TEK PtRu electrocatalyst and the electrocatalyst $PtRu_x$ obtained by spontaneous deposition.

Sample	Pt (nmol/cm^2)	Pt (μg/cm^2)	D_{Nafion} (nm)	J (A/mg)
PtRu	100	19.5	100	0.13
PtRu	25	4.88	50	0.52
PtRu	15	2.93	10	0.82
PtRu	15	2.93	5	0.86
PtRu	15	2.93	1	0.90
PtRu	10	1.95	1	1.05
$PtRu_5$	5	0.95	1	2.58
$PtRu_{10}$	5	0.95	1	2.48
$PtRu_{20}$	5	0.95	1	2.64
$PtRu_{20}$	3	0.57	1	3.74

variation in the smoothness of the catalyst layer, the trend can be clearly seen in the results listed in Table I for E-TEK's PtRu catalysts, the mass-specific current increases several times with the decrease of the Pt loading and Nafion film thickness. For the same 3 μg/cm^2 Pt loading, the data obtained with different Nafion film thicknesses indicate that the effect of the Nafion film becomes negligible below a thickness of 10 nm. Significant irreproducibility was encountered with the electrodes with the 1.95 μg/cm^2 loading due to the problems of obtaining a uniform Pt catalyst layer for such a small amount of the catalyst. The more reliable data are obtained for slightly larger Pt loadings of 3 μg/cm^2 and they represent the activity of the E-TEK PtRu catalyst. Similar measurements were carried out for the catalysts prepared by spontaneous deposition of Pt on Ru. The results for three different Pt:Ru ratios are given in Table I. All the activities are about three times those of the E-TEK PtRu alloy. These data indicate that even for a low Pt coverage on Ru its activity for H_2 oxidation is preserved, which is a prerequisite for an active CO tolerant catalyst.

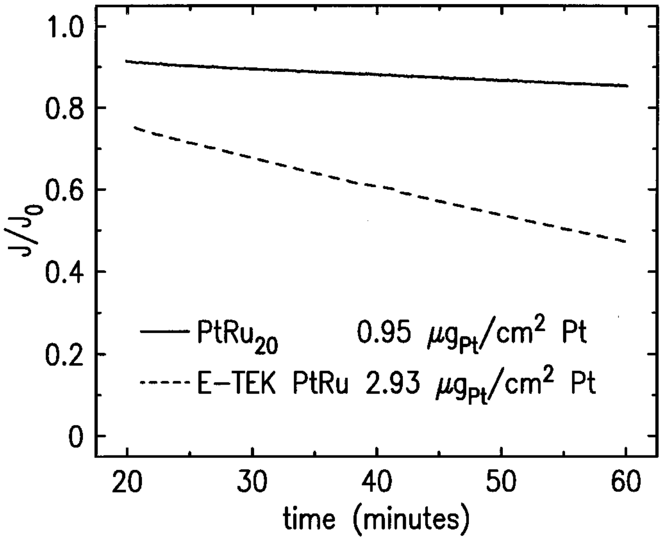

Figure 3. Time dependence of the normalized current at 0.05 V for the oxidation of H_2 with 100 ppm CO in 0.5 M H_2SO_4 at 25°C obtained by using a thin-film rotating electrode at 2500 rpm; j_o is the H_2 oxidation current. During the first 20 min, the current fluctuations (not shown) are large due to a conditioning of the solution.

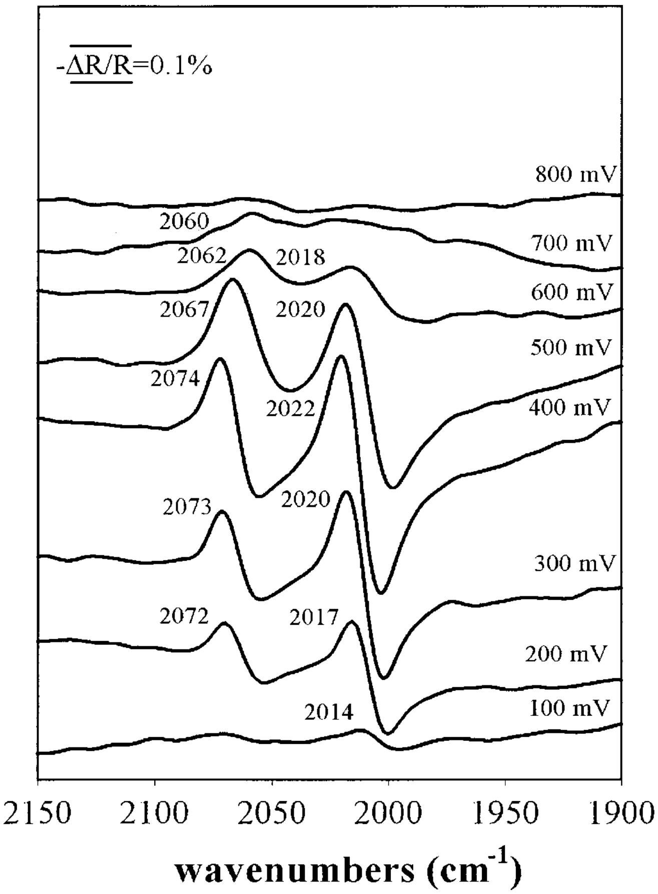

Figure 4. SNIFTIRS spectra for a Ru(0001) electrode with a submonolayer of Pt in a CO-saturated 0.1 M H_2SO_4 solution. The reference spectrum is obtained at 0.075 V and the sample spectra are taken from 0.10 V incremented by 100 mV up to 0.80 V. 8192 scans were coadded in 16 cycles, 512 scans each; the resolution was 8 cm^{-1}. Spectra are offset for clarity.

Figure 3 displays a comparison of the current as a function of time for the oxidation of H_2 with 100 ppm of CO for the $PtRu_{20}$ electrocatalyst, obtained by spontaneous deposition, and for E-TEK's PtRu catalyst with the loadings of 0.95 and 2.93 μg/cm^2 of Pt, respectively. The current for the oxidation of pure H_2, which is the same for both electrocatalysts, was used for the normalization. During the first 20 min (not shown in the graph) the H_2/CO mixture has been bubbled through the solution while the electrodes were subjected to the same polarization and rotation regimes as indicated in the figure. With a very thin (1 nm) Nafion film and low Pt loading, the loss of the activity after 1 h for the spontaneously deposited Pt sample is very small (*ca.* 15%). The loss of activity on the E-TEK's PtRu catalyst is much more pronounced (more than 50%). The significant improvement in CO tolerance shown at room temperature may be further enhanced in the fuel cell operating at the temperature of ~80°C.

The higher CO tolerance of the spontaneously deposited Pt on Ru than that of the Pt-Ru alloy electrocatalyst is likely to be a consequence of the combined electronic effect and the bifunctional mechanism. The latter has often been cited for the Pt-Ru system because of RuOH formation at low potentials, which helps in CO oxidation. At low overpotentials, viz., 50-100 mV, some Ru facets are covered by RuOH, but some can be covered by strongly adsorbed H_2O, as shown in our recent X-ray scattering study for the Ru(0001) surface.[20] These two species are probably playing a role in the adsorption and oxidation of CO. As a consequence of the modified electronic properties of the Pt submonolayer and of the Ru substrate, the bonding of CO with Pt and Ru is expected to be weaker for one, but stronger for the other metal in comparison with their pure phases. The CO stretching frequency is considered a useful probe of modification of surfaces to which CO is adsorbed.

Figure 4 displays SNIFTIR spectra for CO adsorbed on submonolayers of Pt on a Ru(0001) surface as a function of potential. Two bipolar bands have potential-dependent frequencies, which change from 2003 to 2021 cm^{-1} and 2055-2073 cm^{-1}, where the lower and higher frequencies were discerned from the negative and positive lobes, respectively. The first band is associated with CO adsorbed on Ru(0001), but shifted to higher frequencies compared to the band for bare Ru(0001) obtained under same conditions which is between 2000 to 2013 cm^{-1}. The second band is due to CO adsorption on Pt and is red-shifted in comparison to the band for Pt(111) between 2075 and 2080 cm^{-1}.[21] This suggests a decrease of the bond energy of CO to Ru and an increase of the bond energy to Pt. A decrease in frequency of vibration observed for Pt-Ru alloys in comparison to Pt has been interpreted as a sign of a stronger bond of CO to the alloy.[13] Theoretical calculations for Ru on Pt clusters also indicate a small increase in bonding energy (decrease in frequency) and a preferential adsorption of CO on Ru.[22] The argument based on the work function difference between Pt and Ru and the expected charge transfer to Pt supports an increased bond strength to Pt.[13] Therefore, the observed decrease in frequency for the CO-Pt band may not be surprising. It is, however, important that an increase of the band frequency is observed with respect to Ru (2000-2020 cm^{-1}).[23-25] In addition, an increase of the band frequency is observed if the Pt band is compared to a single band for the Pt-Ru (50:50) alloy (2055-2065 cm^{-1}), indicating a weaker bond to Pt in this electrocatalyst than with the PtRu alloy. On the other hand, the temperature programmed desorption (TDS) data for CO on Pt on Ru(0001) indicate a decrease in bonding strength of CO to Pt.[26] The reasons for a difference between the IR and TDS data are not clear at present.

For the electrocatalyst prepared by spontaneous deposition, whose surface is composed of Pt islands and Ru atoms, the above analysis indicates that for the Pt islands on Ru a lower CO coverage can be expected than for the Pt-Ru alloy. Thus, we tentatively propose that as the mechanism of the enhanced CO tolerance of the Pt-Ru electrocatalyst obtained by spontaneous deposition in comparison to that of the Pt-Ru alloy electrocatalyst. Further analysis will be based on the results obtained by application of X-ray absorption spectroscopy and TEM.

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