

Nonalloyed carbon-supported PtRu catalysts for PEMFC applications

Citation for published version (APA):

Papageorgopoulos, D. C., Heer, de, M. P., Keijzer, M., Pieterse, J. A. Z., & Bruijn, de, F. A. (2004). Nonalloyed carbon-supported PtRu catalysts for PEMFC applications. *Journal of the Electrochemical Society*, 151(5), A763-A768. <https://doi.org/10.1149/1.1690286>

DOI:

[10.1149/1.1690286](https://doi.org/10.1149/1.1690286)

Document status and date:

Published: 01/01/2004

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.



Nonalloyed Carbon-Supported PtRu Catalysts for PEMFC Applications

D. C. Papageorgopoulos, M. P. de Heer, M. Keijzer, J. A. Z. Pieterse,
and F. A. de Bruijn^{*,z}

Energy Research Centre of the Netherlands, Fuel Cell Technology, 1755 ZG Petten, The Netherlands

PtRu(1:1)/C catalysts were prepared by a process that was claimed previously to lead to nonalloyed Pt and Ru particles, using two different precursors, Ru nitrosyl nitrate and Ru chloride hydrate. Both X-ray diffraction and characterization by cyclic voltammetry point toward Pt and Ru being present as separate phases in the prepared, nonannealed catalysts. In combination with a high dispersion, this results in proton exchange membrane fuel cell (PEMFC) anode electrocatalysts. These PEMFCs have improved hydrogen oxidation activity and CO tolerance.

© 2004 The Electrochemical Society. [DOI: 10.1149/1.1690286] All rights reserved.

Manuscript submitted June 24, 2003; revised manuscript received November 21, 2003. Available electronically April 14, 2004.

One of the problems confronting proton exchange membrane fuel cell (PEMFC) developers is CO poisoning of the anode. Carbon monoxide, which is a by-product obtained by processing fossil fuels such as methane and gasoline, strongly inhibits hydrogen oxidation on the most commonly used electrocatalyst, platinum, by blocking sites necessary for the reaction to proceed. To overcome this, the ability of the electrocatalyst to poison CO adsorption and/or oxidize it at a low overpotential must be enhanced, while its hydrogen oxidation capability is retained. Bimetallic systems, with Pt as one of the components, give substantial tolerance, compared to platinum alone, to the presence of CO in the fuel stream.¹

PtRu, the current catalyst of choice, exhibits enhanced CO tolerance, which could be ascribed to a decrease in CO binding energy on platinum due to electronic substrate effects² and to the oxidation of chemisorbed carbon monoxide being catalyzed at low potentials by the activation of H₂O.³ The latter derives from the facile formation of the oxygen-containing species, in the form of adsorbed hydroxyl species (OH_{ads}), on oxophilic ruthenium. Surface structure and composition play an important role, especially if one expects oxidation to occur at the interface between the different elements.

Various methods have been employed in preparing PtRu particles, highly dispersed on carbon, for PEMFC applications. Preparatory processes include colloid synthesis⁴⁻⁹ and coprecipitation methods.¹⁰⁻¹⁶ In the latter case, deposition of the metals takes place by reduction of their corresponding salts, with the help of chemical agents or reductive annealing. In all cases, a small particle size, resulting in a high surface area relative to reaction sites, is essential in attaining enhanced activity.

Antolini and Cardellini¹⁴ observed that thermal treatment in an inert atmosphere supported the formation of the alloy on Ketjen black as the carbon support and suggested that the incorporation of Ru atoms in the platinum lattice is diffusion controlled with an activation energy of 34 kJ/mol. Furthermore, Luna *et al.*¹⁵ found the addition of a hydrogen-annealing step beneficial in improving performance. They attributed this to the elimination of impurities in the electrode surface that block the active sites for the reaction, combined with the reduction of high oxidation states of Pt and Ru originally present.

In a process claimed by Degussa AG (presently OMG AG),¹⁶ PtRu/C was prepared by using water-soluble inorganic salts of the noble metals and formaldehyde as the reducing agent. Annealing was avoided, and this resulted in the metals being present in a highly dispersed form on the support without being alloyed to each other, as verified by X-ray diffraction (XRD) analysis. A smaller poisoning effect on the performance was attained in the presence of 100 and

120 parts per million (ppm) of CO in the fuel stream compared to alloyed PtRu/C, which was determined in a fuel cell using an air bleed at the anode.

Recently, this preparation method has been applied by Roth *et al.*¹⁷ The preparation method applied in that study has led to such a low noble metal dispersion that the actual influence of the degree of alloying could not be established.

In the present study, PtRu(1:1)/C, prepared by the method described by Auer¹⁶ with two different ruthenium precursors, has been chemically and electrochemically characterized and tested for applicability as a CO tolerant anode electrocatalyst in the PEMFC. The results obtained were compared to those previously reported and to those from the commercially available catalyst consisting of carbon-supported alloyed PtRu particles.

Experimental

Catalyst preparation and characterization.—All catalysts, supported on carbon Vulcan XC-72 with a 20 wt % metal loading, were prepared by a process relative to the one claimed by Degussa AG.¹⁶ Deposition of the metals from aqueous solution took place by chemical reduction of their corresponding salts, with platinum nitrate (Merck) used as the Pt precursor and formaldehyde as the reducing agent. Samples were prepared with either ruthenium chloride hydrate (RuCl₃·xH₂O, Aldrich) or ruthenium nitrosyl nitrate (Ru(NO)(NO₃)_x(OH)_y, Aldrich) as precursors for Ru. The catalysts prepared from these precursors are referred to throughout this article as PtRu-c and PtRu-n, respectively. The catalysts were dried at 80°C under nitrogen.

An atomic ratio of 1:1 was calculated, and the bulk composition of each of the prepared catalysts was evaluated by energy dispersive X-ray analysis (EDX, Thermo NORAN) in a scanning electron microscope (JEOL JSM-6330F). The measurements confirmed the calculated atomic ratio and total metal weight content of the samples. Trace amounts of Na and Cl were also present, with the latter detected in cases where ruthenium chloride hydrate was used as the precursor. The catalysts were also examined by transmission electron microscopy (TEM, Philips 301); the images revealed similar uniform particle distribution characteristics.

To calculate the fraction of exposed metal atoms of the catalysts, CO pulse chemisorption experiments were carried out with an Altamira AMI-1 apparatus equipped with a thermal conductivity detector. To ensure that the catalyst surface was similar to that in the fuel cell anode, the catalysts were prereduced by heating at 100°C and applying a 30 mL/min flow of dry hydrogen for 17 h. The samples were cooled to 35°C under hydrogen, and CO was pulsed until saturation was reached. The fraction of exposed noble metal atoms FE^{CO} was calculated assuming a adsorption stoichiometry of CO/Pt and CO/Ru of 1:1, leading to

$$FE^{CO} = (pV_{CO}/RT) \times (M_{Pt}/W_{cat}w_{Pt} + M_{Ru}/W_{cat}w_{Ru})$$

* Electrochemical Society Active Member.

^z E-mail: debrijn@ecn.nl

in which

V_{CO} = the total volume of CO adsorbed on the catalyst

$M_{\text{Pt,Ru}}$ = molar mass of Pt and Ru

W_{cat} = total amount of catalyst used in the chemisorption experiment

$w_{\text{Pt,Ru}}$ = weight fraction of Pt and Ru in catalyst.

The XRD analysis was performed at the institute in Eindhoven of the Netherlands Organization for Applied Scientific Research. The analysis was executed with a Philips X'Pert MPD XRD system using Cu K α radiation. Lattice parameter and crystallite size were determined for the PtRu catalysts prepared with the two different Ru precursors. The lattice parameter was determined using silicon as an internal standard, the lattice parameter of which was evaluated by using a certified alumina Standard Reference Material (SRM 676 of The National Institute of Standards and Technology). The particle size was calculated from the XRD patterns using the Scherrer formula and the integral peak width method.

For the cyclic voltammetry (CV) and fuel cell test experiments, propanol-based catalyst inks were prepared with Nafion (5%, EW 1100). For comparison, E-TEK Pt and E-TEK PtRu (1:1), all 20 wt % on Vulcan XC-72, were also used.

CV.—The CV experiments were conducted in 1 N H₂SO₄ (Merck) prepared with Millipore Super-Q water. The setup consisted of a standard electrochemical cell, with the usual three-electrode arrangement, on a computer-controlled Autolab PGSTAT 20 potentiostat/galvanostat (Ecochemie). The working electrode was prepared by the deposition of the catalyst ink under investigation on both sides of a platinum foil (1.5 cm²), leading to a noble metal area of approximately 250 cm², followed by drying in ambient conditions. A platinized Pt square foil (1.5 cm²) was used for the counter electrode, with a platinum surface area of approximately 600 cm². Hg/Hg₂SO₄ (K₂SO₄ saturated) was used as a reference electrode, which has a potential of $E = +0.658$ V vs. the reversible hydrogen electrode (RHE), and all potentials were referred to the RHE.

The samples were electrochemically cleaned in solution by continuous cycling between 18 and 1260 mV (10 cycles) and nitrogen purging at 25°C, which ensured stability in terms of surface area response to potential cycling. No dissolution effects for any of the samples tested were observed after this treatment. Within the first 10 cycles, no structural change in the CO oxidation profile and the PtRu oxide reduction profiles was observed, except for a small decrease in surface area. Only after cycling more than 20 times were the structural changes discernible.

10% CO in argon gas (Scott Specialty Gases) was employed. In each case, the solution was saturated with the gas while the electrode was held at the adsorption potential, which was 18 mV vs. RHE. This adsorption potential is representative for the interaction of CO with a hydrogen-saturated surface in a PEMFC. Solution saturation occurred after dosing for about 35 min. After each dose, bulk CO was removed by bubbling nitrogen through it. Stripping voltammograms were collected between 18 mV (starting potential) and 1.26 V with a scan rate of 5 mV/s for 25°C. Complete oxidation of the adsorbed species was accomplished in a single scan; no oxidation was monitored during the second scan.

Fuel cell membrane electrode assembly (MEA) preparation and experiments.—In all fuel cell experiments reported in this paper, Nafion 105 (Du Pont) was used as a membrane, and prefabricated 0.35 mg Pt/cm² single-sided ELAT gas diffusion electrodes from E-TEK were used as cathode. For the anode, the catalyst ink was applied to an E-TEK single-sided ELAT gas diffusion backing, resulting in an electrode with a low precious metal loading (~0.35 mg/cm²). The electrodes used were impregnated with a 5% Nafion solution, resulting in a Nafion loading of ~1 mg/cm². The MEAs were prepared by hot-pressing the Nafion membrane and the two 7 cm² electrodes together at 130°C and a pressure of 40 bar(g) for 1.5 min.

The MEAs were clamped between two serpentine-machined graphite blocks and connected to the test station. At start-up, a constant voltage of 0.5 V was applied for 18 h, using air (cathode) and hydrogen (anode) humidified at cell temperature by membrane humidification and at a pressure of 1.5 bar. All experiments were performed at 80°C. To examine CO tolerance, the fuel cells voltage drop over the electronic load was kept constant at 0.5 V, while the current density was measured for several CO concentrations in pure H₂, with performance data obtained in the steady state.

Results and Discussion

Catalyst characterization: XRD and CO pulse chemisorption experiments.—XRD is an experimental method used to reveal information on the bulk structure of the catalyst and its support. For platinum and ruthenium, XRD patterns display reflection characteristics of a face-centered cubic (fcc) and a hexagonal close-packed (hcp) crystal structure, respectively. In the bulk PtRu alloy, for Ru atomic fractions of up to about 0.62, Pt and Ru can form an alloy with Ru atoms replacing Pt atoms in a fcc structure.¹⁸ Above 0.62 Ru atomic fraction, another alloy can be formed in which the ruthenium atoms are replaced by Pt in an hcp structure. The composition of the alloy can be determined by the variation of the crystal lattice, which manifests itself in a shift of the Pt reflections, as observed for both unsupported¹⁹ and carbon-supported solutions.²⁰

Figure 1 depicts the XRD patterns of PtRu/C prepared with a ruthenium nitrosyl nitrate precursor (PtRu/C-n) and with hydrated RuCl₃ (PtRu/C-c), mixed with Si as an internal standard. While the very sharp reflections are due to this internal standard, the catalyst exhibits broad reflections, with the first one near 26° coming from the amorphous carbon support. The large extent of peak broadening observed is a result of the very small crystallite size of the “as-prepared” material. This reduces the accuracy of the determination of both lattice parameter and crystallite size. The lattice parameter for both samples was estimated at 0.394 nm, with a standard deviation of 0.02 and 0.03 nm for the two samples. The value for pure Pt is 0.3923 nm and for Pt/C, 20 wt % by E-TEK was estimated at 0.39155 nm.²¹ For PtRu in the alloyed phase, the lattice parameter for Pt would have been shifted to 0.3884 nm.¹²

The presence of crystallite Ru in the samples could not be excluded, because the strongest reflections of Pt and Ru overlap. However, because of the broadening and because the signal-to-noise ratio was too low, it could not be identified either. A definite distinction between nonalloyed Pt and Ru and alloyed PtRu would not be accurate. The crystallite size was estimated at 0.9 and 1.1 nm for PtRu/C-n and PtRu/C-c, respectively, with both samples being at least in the 0.6–1.5 nm range.

XRD results from experiments conducted at Degussa AG¹⁶ on PtRu/C prepared with the same method gave a similar estimate for the particle size, but with reflections from both Pt and Ru claimed to be clearly visible in the spectrum. No shift in the Pt reflections was detected, indicating that an alloy was not produced. The Pt crystallite size was estimated at or less than 1.5 nm and that of Ru below 1 nm. In another study of PtRu/C electrocatalysts by Roth *et al.*,²² prepared in a similar fashion with formaldehyde as the reducing agent, but with hexachloroplatinic acid as the platinum precursor, Ru reflections were observed only after heat-treatment in a nitrogen environment. It was proposed that this may be due to recrystallization or growth of individual ruthenium particles. A lattice parameter of 0.391 nm was estimated with a particle size of 7 nm. The formation of irregular agglomerates on the carbon support was also observed by TEM.

The fraction of exposed metal atoms (also called metal dispersion) for the catalysts were determined by CO pulse chemisorption, one of the most straightforward ways to measure adsorbate uptake by a metal surface.^{23,24} Figure 2 shows the amount of CO per pulse as measured at the outlet for the three catalyst samples, *i.e.*, the two prepared catalysts and PtRu/C (E-TEK) for comparison. Although for all three samples the sequence of CO pulses ends with saturation of the surface, the prepared catalysts show a peculiarity in terms of

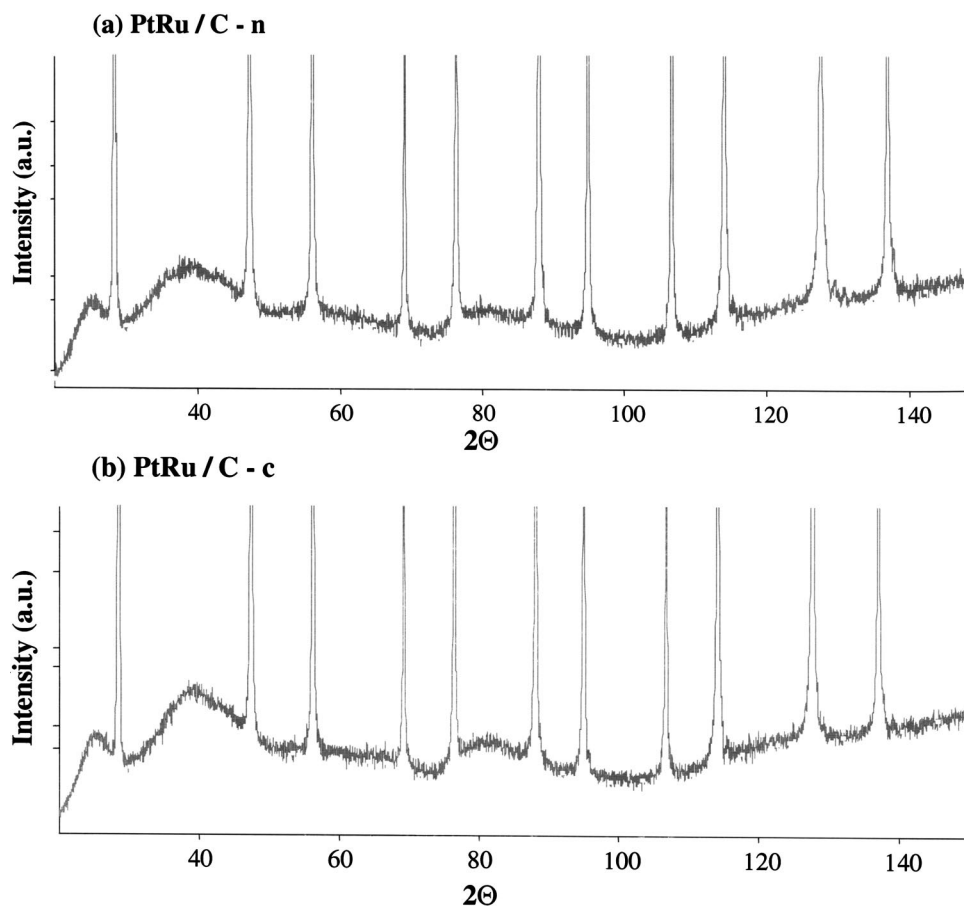


Figure 1. Fitted XRD patterns of PtRu/C prepared with (a) a ruthenium nitrosyl nitrate precursor and (b) hydrated RuCl_3 , mixed with Si as an internal standard.

CO sticking with increasing coverage compared to the commercially available PtRu alloy. For the latter, the sticking coefficient decreases with consecutive pulses, as expected, but for the prepared catalysts, there is an initial increase in uptake, up to a certain coverage, above which there is a decrease until saturation. This effect was very reproducible, taking various fresh samples of the same catalyst batch.

It seems that the CO sticking coefficient exhibits coverage-dependent characteristics, with adsorption enhanced as the CO adlayer builds up on the particle's surface, up to a certain critical coverage, after which the uptake decreases from the limitation of available vacant sites. Adsorbed CO could modify the chemisorption potential by increasing the binding energy, or it could induce struc-

tural changes that increase surface area by particle reconstruction. Alternatively, a higher hydrogen saturation coverage, for the prepared catalysts, would result in a lower vacant site availability initially, which would in turn manifest in a delay in hydrogen displacement. Carbon monoxide pulse chemisorption experiments on 20 wt % Pt/C and Ru/C, supplied by E-TEK, showed coverage-dependent uptake characteristics similar to those of PtRu/C (E-TEK).

PtRu/C-n gives the fraction of exposed metal atoms as 71% compared to 41% for PtRu/C-c, which is higher for both than the 29% calculated for PtRu/C (E-TEK). For monometallic Pt/C and Ru/C, the fractions of exposed metal atoms were calculated at 24 and 11%, respectively. Thus, evidently, apart from the small crystallite size, a relatively high fraction of exposed metal atoms compared to PtRu/C (E-TEK) is attained with the prepared catalysts, which may manifest itself in favorable hydrogen oxidation and carbon monoxide tolerance characteristics useful for PEMFC applications.

Electrochemical characterization: CV.—CV is probably the most widely used technique for the electrochemical characterization of catalysts. Figure 3 compares the voltammograms of PtRu/C-n, PtRu/C-c with that of PtRu/C (E-TEK). The voltammograms have been normalized to their respective metal content, as given by the weight of the dried inks applied to the electrode surface. The hydrogen region, from 0 to ~ 0.33 V vs. RHE, corresponding to the reductive adsorption of protons in the cathodic scan and the subsequent oxidation of the hydrogen adatoms in the anodic scan, seems to be slightly more defined for the prepared catalysts than for PtRu/C (E-TEK). This is expected from the high degree of alloying in the latter. Moreover, the nonannealed catalyst particles exhibit a higher electrochemical surface area, as seen from the increase of the charges both in the hydrogen and oxide regions. This is more pronounced for PtRu/C-c, especially from the enhanced oxide formation-reduction charges. There are small deviations in particle

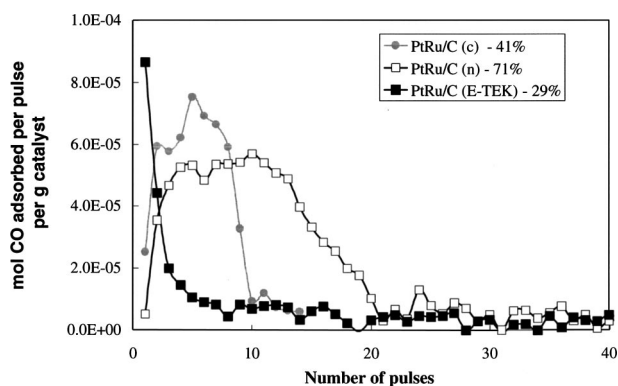


Figure 2. Peak areas of nonchemisorbed CO with consecutive pulses from PtRu/C (E-TEK) and PtRu/C prepared with Ru nitrosyl nitrate and hydrated RuCl_3 precursors.

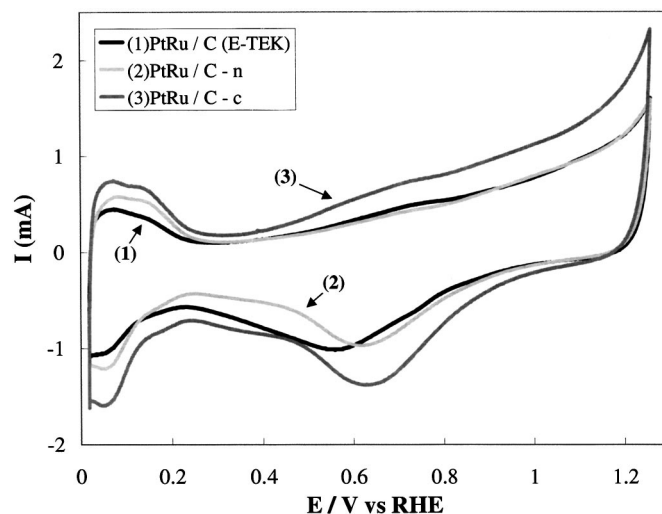


Figure 3. CV of carbon-supported PtRu-n, PtRu-c, and PtRu (E-TEK) in 1 N H₂SO₄ at 25°C. The spectra have been normalized to their respective catalyst metal content. Scanning rate $\nu = 5$ mV/s.

size between the catalysts, with a crystallite size of 2-4 nm for PtRu/C (E-TEK),²⁵ and the prepared PtRu/C particles reveal a rougher surface and, for PtRu/C-c, an enhanced ability to attract more oxygenated species. Note that, apart from trace amounts of Na present in both PtRu/C-n and PtRu/C-c, a product of the preparation process, Cl was also present in PtRu/C-c, as observed by EDX. Compared to the PtRu/C (E-TEK) sample, the oxide reduction peak is shifted to a higher potential, 0.6 V vs. RHE, corresponding to the potential for oxide reduction of pure platinum. Especially in the PtRu/C-c sample, a second oxide reduction feature can be discerned at 0.3 V. This reduction peak at 0.3 V coincides with the reduction potential for pure ruthenium.²⁶ For the PtRu-E-TEK catalyst, both reduction peaks are merged to a single reduction peak, as is expected for an alloyed system.

Anodic stripping voltammetry was utilized for the study of the electro-oxidation characteristics of adsorbed CO. Figure 4 shows the CO stripping voltammetry on all three PtRu/C samples, following carbon monoxide saturation at 18 mV vs. RHE and subsequent purging of the solution with N₂, at 25°C. At the adsorption potential of 18 mV, the coverage of adsorbed hydrogen is unity. Upon CO saturation of the solution, CO displaces virtually all of the hydrogen

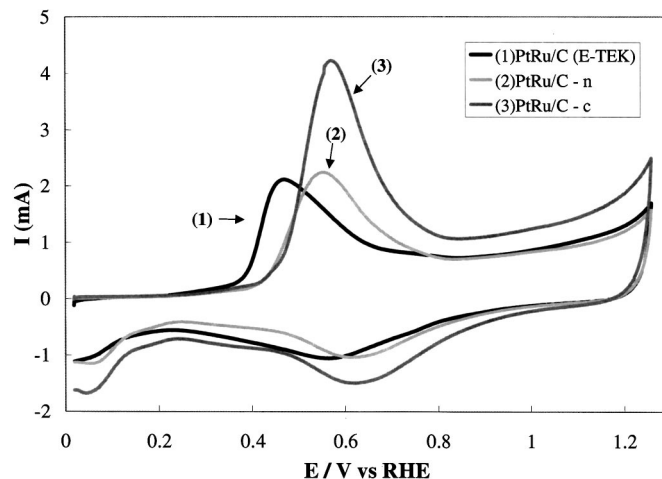


Figure 4. CV of carbon-supported PtRu-n, PtRu-c, and PtRu (E-TEK) following CO saturation in 1 N H₂SO₄ at 25°C. Scanning rate $\nu = 5$ mV/s.

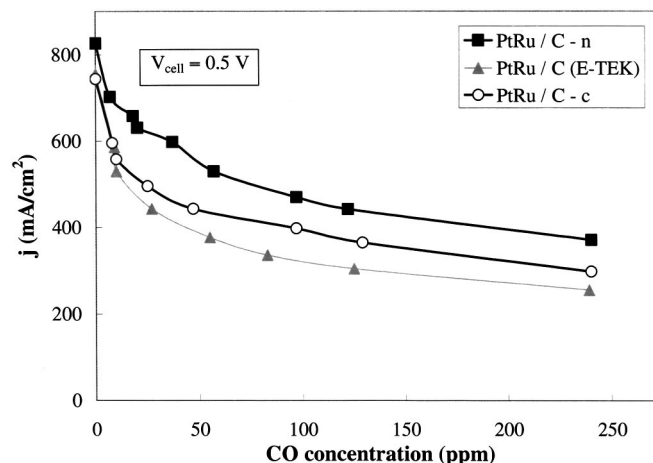


Figure 5. Current density vs. CO concentration for cells operated with anode catalysts consisting of carbon-supported PtRu-n, PtRu-c, and PtRu (E-TEK) at a pressure of 1.5 bar and a cell voltage of 0.5 V. $T_{\text{cell}} = T_{\text{hum}} = 80^\circ\text{C}$.

from the surface, as seen by the total suppression of the hydrogen adsorption-desorption charges. The peak potential (E_p) for CO oxidation from PtRu/C lies at a much lower value than that for Pt/C,²⁷ an outcome of the higher activation of H₂O and a weakening of the CO-metal bond on the bimetallic surface.

Interestingly, the oxidation of carbon monoxide is delayed for the prepared samples. Whereas there is only a minor deviation in E_p values from PtRu/C-n and PtRu/C-c, these lie 85-100 mV higher than that from PtRu/C (E-TEK), while the onset of oxide formation and thus probably also the onset of water activation is the same, as seen from the clean voltammograms (Fig. 3). These observations are in line with those by Gasteiger *et al.*,^{26,28,29} who measured the activity of Pt, Ru, and PtRu electrodes for CO oxidation. The CO oxidation potential is increased in the following order: alloyed PtRu, pure Ru, and pure Pt. The oxidation potential in Fig. 4 of this study coincides with the oxidation potential of CO on pure Ru in the study by Gasteiger *et al.*^{26,28,29} CO oxidation on Pt would occur at potentials approximately 100 mV higher. This is further evidence of Pt and Ru atoms in the prepared catalysts not being in the alloyed state.

Based on the broad oxidation peak for the prepared catalysts, no discrimination can be made between CO being oxidized on both Pt and Ru, or only on Ru sites. Comparing Fig. 4 to the data of Gasteiger *et al.*,^{26,28,29} the latter possibility seems more plausible, as Ru and Pt are deposited on the catalyst in equal amounts, and the Ru profile dominates in Fig. 4, with a small shoulder being present on the high potential side.

Fuel cell tests.—The influence of CO on MEAs with anodes consisting of PtRu/C-n, PtRu/C-c, and PtRu/C (E-TEK) was tested directly under PEMFC conditions. The effect of CO on the cell performance is seen in Fig. 5, where the current density is plotted against CO concentration with the cell voltage set at 0.5 V at 80°C. Anodes consisting of the prepared catalysts gave higher fuel cell current densities in the presence of CO in the fuel stream.

The current density attained by PtRu/C-n, with pure hydrogen as the fuel, was slightly higher than those from both PtRu/C-c and PtRu/C (E-TEK), in agreement with the dispersion measurements presented earlier. The higher electrochemical surface area observed in CV for PtRu/C-c does not result in larger hydrogen oxidation currents.

Both carbon-supported PtRu-n and PtRu-c show enhanced tolerance, as evident for CO concentrations above 20 ppm, than the commercially available alloyed system. The catalyst prepared with ruthenium nitrosyl nitrate as the precursor exhibits a somewhat improved performance on average compared to the one prepared with

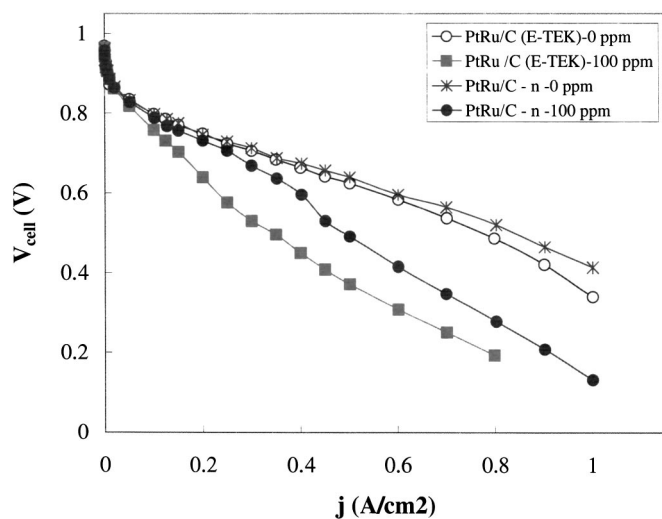


Figure 6. Current density-cell voltage curves of cells operated on pure H_2 and H_2 containing 100 ppm CO, with anode catalysts consisting of carbon-supported PtRu-n and PtRu (E-TEK) at a pressure of 1.5 bar. $T_{cell} = T_{hum} = 80^\circ C$.

ruthenium chloride hydrate. These results have been duplicated and additionally verified, as with the characterization experiments, with tests conducted with a second batch of prepared catalysts.

Prepared carbon-supported PtRu exhibits improved tolerance over a series of cell voltages, as seen in the current density-cell voltage plots shown in Fig. 6. There is an evident enhancement in the ability of the anode to tolerate carbon monoxide, as observed from the j/V curves with 100 ppm CO. The results are in qualitative agreement, in terms of the prepared catalysts' superiority to PtRu/C (E-TEK), with results from experiments conducted, for the same catalyst system, at Degussa AG (OMG AG).¹⁶ The voltage drop at constant current density observed in their study was smaller, and this could be attributed primarily to the addition of air at the anode side (called the air-bleed).

The two constituting metals in the prepared bimetallic system are not, or are poorly, alloyed to each other, as assumed by the XRD results presented here and more definitely indicated from those presented elsewhere.¹⁶ The bifunctional mechanism requires an abundance of Pt-Ru interfacial sites with alloy formation not appearing as a prerequisite in achieving enhanced CO tolerance. Moreover, it is possible that the whole process on an alloy could be hindered through the prevalence of surface segregation effects, with the surface of the alloyed particles being enriched in platinum with a lack of sufficient ruthenium sites to produce the oxygenate species. For nonalloyed PtRu to render enhanced CO tolerance compared to platinum, the diffusion of the reactants must take place at a rate fast enough compared to the required hydrogen oxidation rate. This means that either the oxidant produced at the Ru sites should diffuse to platinum sites that lie further away, as was suggested to explain the existence of a second oxidation peak, at higher potential, for Ru modified Pt(111).³⁰ However, CO adsorbed on Pt could diffuse to the OH-containing Ru sites.¹⁷ As was calculated by Koper *et al.*,² both CO and OH are bonded more strongly on Ru than on Pt. For separate Pt and Ru phases, CO adsorbed on Pt would thus diffuse to the most proximate Ru site, making the Pt site available for H_2 -adsorption and subsequent oxidation.

The enhanced CO tolerance observed for both PtRu/C-n and PtRu/C-c, in comparison to the commercially available electrocatalyst, must be attributed to the higher dispersion measured in combination with Pt and Ru being present as separate phases as seen in XRD and CV analyses. Besides, CO pulse chemisorption experiments indicate behavior that clearly differs from the alloyed PtRu catalysts. The preparation process, as claimed by Degussa AG, gives

PtRu/C with superb crystallite size and particle surface area. The better performance of Pt and Ru in the nonalloyed state vs. the alloyed state can only be explained by the fact that hydrogen oxidation on Pt is faster than on PtRu. This is in line with recent experiments and part of the conclusions reported by Wang *et al.*³¹ Wang *et al.* prepared small Pt clusters on Ru nanoparticles, resulting in Pt and Ru in the nonalloyed state. They too ascribe the improved CO tolerance to the retained hydrogen oxidation capability of Pt in the nonalloyed state, combined with an extremely small Pt particle size, rendering a relatively high specific area.

Carbon monoxide fully saturates all samples tested in CV. This should be regarded as the state at equilibrium and does not necessarily reflect the steady-state situation in the fuel cell. In the fuel cell experiments, a steady state exists in which the CO coverage clearly must be lower than unity, as otherwise no current would be delivered by the fuel cell at cell voltages between 0.7-0.8 V, where the anode potential is below the potential at which the onset of CO oxidation occurs. As seen in Fig. 6, the difference in current-voltage characteristics at low current densities is very small for hydrogen and hydrogen/CO mixtures, due to the fact that at these low current densities the amount of platinum sites needed to generate the current is small enough and is apparently available and not dependent on CO oxidation rates. However, remember that the lower than unity coverage by CO at steady state is the result of the conditions in the fuel cell: the relative concentrations of H_2 and CO, their relative rates of adsorption, their adsorption stoichiometries, and their relative oxidation rates mean that, at a steady state, which is more or less the case in the fuel cell I/V curve, the CO coverage is less than unity. The fact that CO does adsorb more strongly on Ru and the postulate that hydrogen oxidation takes place at a faster rate on nonalloyed Pt than on Pt alloyed with Ru lead to a higher steady-state current density in the fuel cell than expected from CV experiments and the bifunctional theory by itself.

For the two Ru precursors tested, ruthenium nitrosyl nitrate appears to be better than ruthenium chloride hydrate. Trasatti and co-workers³² found the oxygen evolution reaction to be kinetically enhanced for RuO_2 from $Ru(NO)(NO_3)_3$ compared to RuO_2 from hydrated $RuCl_3$, and more recently a high surface charge, which is proportional to the surface concentration of active sites, is associated with RuO_2 from nitrate.³³ PtRu/C-c is more contaminated due to the presence of trace amounts of chlorine. The higher activity of PtRu/C-n to PtRu/C-c, in relation to CO tolerance, seems to stem from the higher dispersion characteristics, as determined by CO-chemisorption experiments, achieved when Ru nitrosyl nitrate is used. The apparent higher surface area for PtRu/C-c as measured in the CV experiments could stem from the fact that chloride is more easily removed from the surface in a clean, chloride-free electrolyte than in a gas-phase environment as present in the CO chemisorption and fuel cell experiments.

Conclusions

The method used for the preparation of PtRu catalysts leads to Pt and Ru being present as separate, nonalloyed phases. Although there is no direct evidence in this study for this statement, XRD, CV, and CO chemisorption indicate that the prepared samples differ clearly from PtRu/C commercially available from E-TEK. Besides, more direct evidence is delivered by others using the same preparation procedure.

CV experiments indicate all the CO to be oxidized on Ru. The CO adsorbed on platinum sites needs to diffuse from platinum to ruthenium, making these platinum sites available for the oxidation of hydrogen. In order for the CO oxidation at Ru to take place at a considerable rate, the platinum and ruthenium sites must be close enough together, but apparently not in the alloyed state. In combination with a very high dispersion in the prepared, nonalloyed catalysts, this results in anode electrocatalysts with improved hydrogen oxidation activity in the presence of carbon monoxide in the fuel stream, as is evident from fuel cell test experiments.

As the oxidation of carbon monoxide on the prepared catalysts actually takes place at higher potentials than on the alloyed catalysts, in combination with the full saturation of both surfaces with CO, this positive effect can only stem from the higher hydrogen oxidation activity of nonalloyed platinum compared to that of platinum alloyed with ruthenium.

The Netherlands Energy Research Foundation assisted in meeting the publication costs of this article.

References

1. T. R. Ralph and M. P. Hogarth, *Platinum Met. Rev.*, **46**, 117 (2002).
2. M. T. M. Koper, T. E. Shubina, and R. A. van Santen, *J. Phys. Chem. B*, **106**, 686 (2002).
3. M. Watanabe and S. Motoo, *J. Electroanal. Chem. Interfacial Electrochem.*, **60**, 267 (1975).
4. H. Bönemann, W. Brijoux, R. Brinkmann, E. Dinjus, T. Jousen, and B. Korall, *Angew. Chem.*, **103**, 1344 (1991).
5. T. J. Schmidt, M. Noeske, H. A. Gasteiger, R. J. Behm, P. Britz, W. Brijoux, and H. Bönemann, *Langmuir*, **13**, 2591 (1997).
6. T. J. Schmidt, M. Noeske, H. A. Gasteiger, R. J. Behm, P. Britz, and H. Bönemann, *J. Electrochem. Soc.*, **145**, 925 (1998).
7. U. A. Paulus, U. Endruschat, G. J. Feldmeyer, T. J. Schmidt, H. Bönemann, and R. J. Behm, *J. Catal.*, **195**, 383 (2000).
8. T. H. Galow, A. K. Boal, and U. M. Rotello, *Adv. Mater. (Weinheim, Ger.)*, **12**, 576 (2000).
9. M. Götz and H. Wendt, *Electrochim. Acta*, **43**, 3637 (1998).
10. M. Watanabe, M. Uchida, and S. Motoo, *J. Electroanal. Chem. Interfacial Electrochem.*, **229**, 395 (1987).
11. K. Tsurumi, T. Nakamura, and A. Sato, U.S. Pat. 4,956,331 (1990).
12. V. Radmilović, H. A. Gasteiger, and O. N. Ross, Jr., *J. Catal.*, **154**, 98 (1995).
13. J. B. Goodenough, M. Hamnett, B. J. Kennedy, R. Manoharan, and S. A. Weeks, *Electrochim. Acta*, **35**, 199 (1990).
14. E. Antolini and F. Cardellini, *J. Alloys Compd.*, **315**, 118 (2001).
15. A. M. Castro Luna, G. A. Camara, V. A. Paganin, E. A. Ticianelli, and R. R. Gonzalez, *Electrochem. Commun.*, **2**, 222 (2000).
16. E. Auer, A. Freund, T. Lehmann, K. A. Starz, R. Schwarz, and U. Stenke, U.S. Pat. 6,007,934 (1999).
17. C. Roth, N. Martz, F. Hahn, J.-M. Léger, C. Lamy, and H. Fuess, *J. Electrochem. Soc.*, **149**, E433 (2002).
18. H. A. Gasteiger, P. N. Ross, Jr., and E. J. Cairns, *Surf. Sci.*, **293**, 67 (1993).
19. D. Chu and S. Gilman, *J. Electrochem. Soc.*, **143**, 1685 (1996).
20. E. Antolini, L. Giorgi, F. Cardellini, and E. Passalacqua, *J. Solid State Electrochem.*, **5**, 131 (2001).
21. E. Antolini, F. Cardellini, L. Giorgi, and E. Passalacqua, *J. Mater. Sci. Lett.*, **19**, 2099 (2000).
22. C. Roth, N. Martz, and H. Fuess, *Phys. Chem. Chem. Phys.*, **3**, 315 (2001).
23. J. J. F. Scholten, A. P. Pijpers, and A. M. L. Hustings, *Catal. Rev. - Sci. Eng.*, **27**, 151 (1985).
24. F. A. de Bruijn, B. F. M. Kuster, and G. B. Marin, *Appl. Catal., A*, **145**, 351 (1996).
25. E-TEK Catalogue, E-TEK Division of De Nora N. A., Inc., Somerset, NJ (2001).
26. H. A. Gasteiger, N. Markovic, P. N. Ross, Jr., and E. J. Cairns, *J. Phys. Chem.*, **99**, 8290 (1995).
27. D. C. Papageorgopoulos, M. Keijzer, and F. A. de Bruijn, *Electrochim. Acta*, **48**, 197 (2002).
28. H. A. Gasteiger, N. M. Markovic, and P. N. Ross, Jr., *J. Phys. Chem.*, **99**, 16757 (1995).
29. H. A. Gasteiger, N. Markovic, P. N. Ross, Jr., and E. J. Cairns, *J. Phys. Chem.*, **98**, 617 (1994).
30. J. C. Davies, B. E. Hayden, D. J. Pegg, and M. E. Rendall, *Surf. Sci.*, **496**, 110 (2002).
31. J. X. Wang, S. R. Brankovic, Y. Zhu, J. C. Hanso, and R. R. Adžić, *J. Electrochem. Soc.*, **150**, A1108 (2003).
32. S. Ardizzone, M. Falcicola, and S. Trasatti, *J. Electrochem. Soc.*, **136**, 1545 (1989).
33. E. Fachinotti, E. Guerrini, and S. Trasatti, *Abstract Proceedings of the 4th International Conference on Electrocatalysis (ECS'02)*, 23-25 Sept 2002, Como, Italy, p. 140 (2002).