

# Characteristics of platinum-based electrocatalysts for mobile PEMFC applications

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## Abstract

Platinum-based electrocatalysts play an important role in the development of high performance PEMFC stacks for mobile applications. This paper reviews objectives, development work, and results of a Research and Development Program funded by the German Ministry of Education, Science, Research and Technology (BMBF) to develop the basic technology as well as components for mobile PEMFC applications. In the framework of this program, Degussa-Hüls developed precious metal-based electrocatalysts for operation under practical reformat/air PEMFC conditions which yield high power densities up to 0.5 W/cm<sup>2</sup> at low total platinum loadings of less than 0.5 mg Pt/cm<sup>2</sup>. A CO-tolerant anode electrocatalyst, exhibiting a CO-tolerance of 100 ppm CO, was developed and characterized. The features of the new electrocatalyst materials were verified by DaimlerChrysler in a 2.7 kW PEMFC stack at the end of the program. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Polymer electrolyte membrane fuel cell (PEMFC); Electrocatalyst; Platinum; Reformat; CO-tolerance; Membrane-electrode-assembly (MEA)

## 1. Introduction

Cost reduction of polymer electrolyte membrane fuel cell (PEMFC) stack components such as electrocatalysts, ionomer membranes, membrane-electrode-assemblies (MEAs) and bipolar plates is an important task to be solved for the commercial application of PEMFC technology in the future, particularly for mobile applications. The development of high performance electrocatalysts plays a vital role in this context [1].

Electrocatalysts for PEMFC have to fulfill various requirements: Primarily, a high intrinsic activity is necessary for the electrochemical oxidation of hydrogen at the anode as well as for oxygen reduction at the cathode of the PEMFC. High performance cathode electrocatalysts must improve the slow oxygen reduction kinetics by reducing the high overpotential of this 4-electron-reaction. Anode electrocatalysts catalyse the hydrogen oxidation process,

and, in addition to that, should be resistant to poisoning caused by CO, CO<sub>2</sub> and other contaminants in the reformat feed gas.

Furthermore, good electrical conductivity of the catalyst materials is required to enable the electron transfer between the PEMFC electrodes. As a consequence, conductive supports such as carbon blacks have to be used.

For cost reasons, the total Pt-loading of PEMFC-stacks and MEAs has to be as low as possible; a Pt consumption of less than 0.5 g Pt/kW should be an attainable target for the future [2]. Low Pt consumption and improved cell performance are crucial, however there should be no sacrifice in cell and stack operating lifetime (4000 h minimum for mobile applications).

Last but not least, the electrocatalysts must be tailored for environmentally safe, high volume manufacturability and should be suitable for precious metal recycling processes at the end of the product lifetime.

The overall goal of the research program was to develop the basic technology and components for the PEMFC for use in automotive applications. The program objectives were defined and agreed upon by the participating companies (DaimlerChrysler, Siemens, Hoechst/Aventis, Her-

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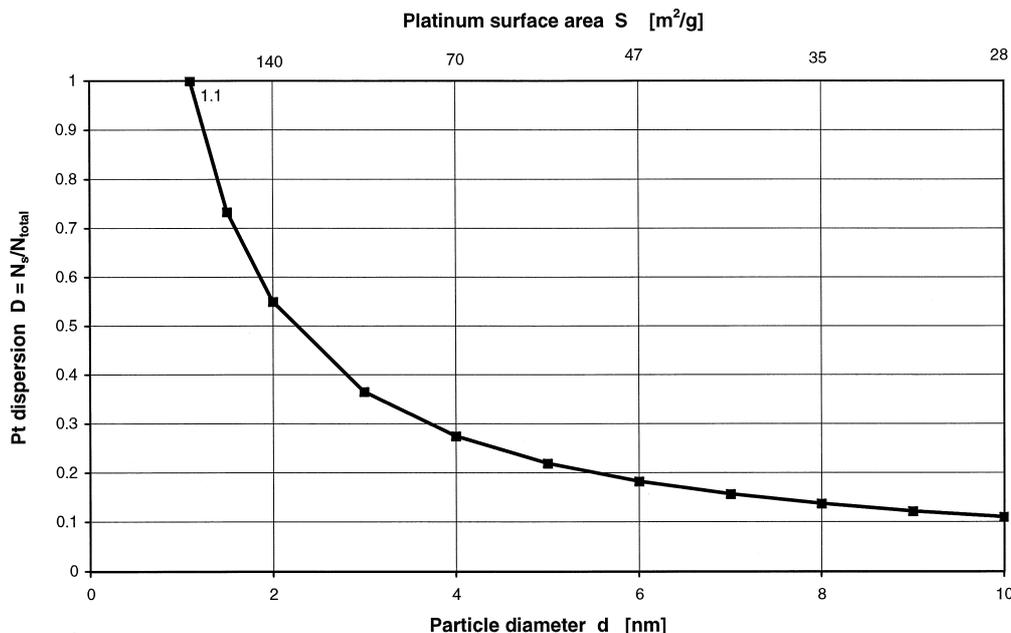


Fig. 1. Correlation of Pt dispersion  $D$  vs. particle diameter and Pt surface area.

aeus, BASF and Degussa-Hüls) at the beginning of the work [3]. The sub-task of Degussa-Hüls was to develop electrocatalysts materials to meet the following performance criteria in PEMFC single cells and stacks:

Power density	
- PEMFC single cell and stack	> 0.4 W/cm <sup>2</sup>
Platinum loading	
- per electrode	< 0.4 mg/cm <sup>2</sup>
- total loading	< 0.8 mg/cm <sup>2</sup>
CO-tolerance	
- reformate/air mode	> 40 ppm

The new components and materials developed during the course of the work had to be evaluated by the system manufacturers in a PEMFC stack in the 2–5 kW size at the end of the program.

## 2. Experimental

Carbon-black-supported, precious metal-based electrocatalysts as well as membrane-electrode-assemblies (MEAs) were prepared according to Degussa's proprietary methods [4,5]. Structural information about the electrocatalysts were received from X-ray diffraction analysis (XRD) and transmission electron microscopy (HRTEM; JEOL 200 keV). Electrochemical catalyst characterisation was done by cyclic voltammetric methods (CV, ECA) and CO-stripping experiments. MEAs were characterized by single-cell testing in PEMFC hardware with active cell areas of 25 cm<sup>2</sup> (5 × 5 cm). Operating conditions were 3 bar<sub>abs</sub> pressure at anode and cathode, cell temperature 75°C and 1.5/2.0 anode/cathode stoichiometries. Stan-

dard ionomer membrane materials (DuPont Nafion<sup>®</sup> 115 and 112) were used for MEA manufacture.

## 3. Results and discussions

### 3.1. Pt/C-electrocatalysts

For PEMFC, platinum is used either as a fine powder ("platinum black") or supported on a carbon black mate-

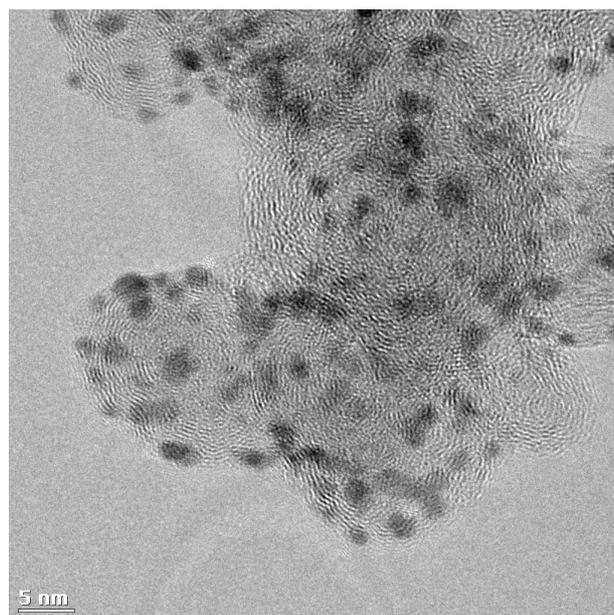


Fig. 2. High resolution (HRTEM) picture of carbon supported electrocatalyst FH 901R/D, 20% PtRu.

Table 1  
Characteristic data of Pt/C-electrocatalysts

Type	F901 KR/D 10% Pt	F901 KR/D 20% Pt	F901 KR/D 30% Pt
Pt content (wt.%)	10.0 ± 0.5	20.0 ± 0.5	30.0 ± 0.5
Particle diameter (XRD, nm)	2.0 ± 0.5	2.5 ± 0.5	3.5 ± 0.5
Pt surface area ( $S = 280/d$ , m <sup>2</sup> /g)	140	112	80
Pt-surface area (TEM, m <sup>2</sup> /g)	140–160	90–110	70–90
Electrochemical surface area (ECA, m <sup>2</sup> /g)	120–140	90–110	60–80
Apparent density (g/l)	300 ± 50	350 ± 50	400 ± 50

rial. With carbon supported electrocatalysts instead of conventional Pt blacks, it is possible to reduce the Pt-loading of electrodes and MEAs roughly by one order of magnitude. Since the Pt particles are fixed on the carbon support, a higher Pt surface area can be obtained compared to the Pt black materials.

Important characteristic data of electrocatalysts are the degree of Pt dispersion  $D$ , the particle diameter  $d$  and the specific Pt surface area  $S$ . Theoretically, the platinum dispersion  $D$  is given by the number of atoms at the surface of the crystallite ( $N_s$ ) vs. the total number of atoms of the particle ( $N_{tot}$ ) and can be estimated for a given particle size  $d$  by the following equation [6]:

$$D = N_s/N_{tot} = 1.1/d.$$

In order to achieve a Pt dispersion of 50%, crystallites with a diameter of approx. 2.2 nm must be deposited on the support material.

The maximum specific surface area of the Pt particles can be calculated [7] by the equation:

$$S = 6/(\rho_{Pt} d) = 280/d \text{ (m}^2/\text{g)}$$

with

$$\rho_{Pt} = 21.45 \text{ g/cm}^3$$

and

$d$  = particle diameter (in nm).

The correlation of the parameters  $D$ ,  $S$  and  $d$  is depicted in Fig. 1. As can be seen from this diagram, a decrease of the Pt particle diameter from 4 to 2 nm causes the Pt surface area  $S$  to increase by a factor of 2. This underlines the importance of Pt particle size in electrocatalyst performance. In Fig. 2, a high resolution (HRTEM) picture of a carbon supported Pt electrocatalyst (Type FH 901R/D, 20 wt.% PtRu) is shown. Precious metal nanoparticles with a medium size of 2.5 nm are homogeneously distributed over the surface of the carbon black particles.

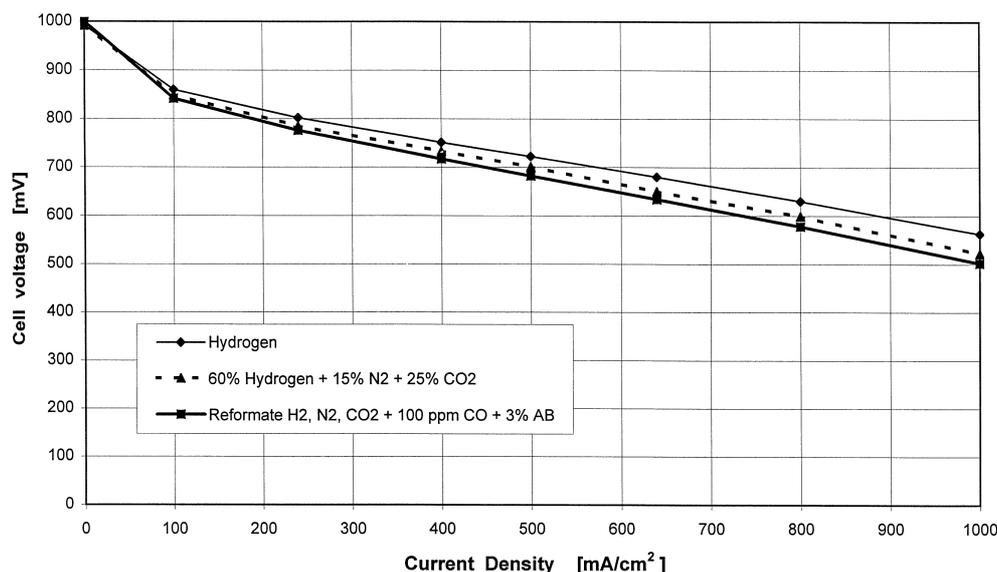


Fig. 3. CO-tolerance of anode electrocatalyst FH 901R/D, 20% PtRu; PM loading (anode): 0.25 mg Pt/cm<sup>2</sup> + 0.17 mg Ru/cm<sup>2</sup>; total Pt loading: 0.5 mg/cm<sup>2</sup>; reformate/oxygen (3/3 bar<sub>abs</sub>);  $T = 75^\circ\text{C}$ ; active cell area 25 cm<sup>2</sup>.

Table 2  
Characteristic data of anode electrocatalyst

Type	FH 901 R/D, 20% PtRu
Pt content (wt.%)	$13.2 \pm 0.5$
Ru content (wt.%)	$6.8 \pm 0.5$
Atomic ratio Pt:Ru	1:1
Precious metal surface area (TEM, $\text{m}^2/\text{g}$ )	90–110
CO stripping peak potential (mV)	665
Apparent density ( $\text{g}/\text{l}$ )	$300 \pm 50$

Electrocatalysts are embedded in the reaction layers of the membrane-electrode-assembly. A high catalyst performance is obtained by a maximum utilization of active electrocatalyst sites, which, in turn, must have effective simultaneous contact to protons, electrons and the gaseous reactants. In order to meet the requirements of various MEA manufacturing methods, a range of Pt/C electrocatalysts with Pt-loadings of 10, 20 and 30 wt.% was developed. The typical data of these materials are summarized in Table 1.

As the Pt loading on the carbon support increases, the particles get larger and, as a consequence, the available Pt surface area is decreasing. This correlation is shown in Table 1: the Pt particle size is growing from 2 nm (10 wt.% Pt/C) to 3.5 nm (30 wt.% Pt/C) whereas the Pt surface area (measured by TEM) is reduced from 140–160  $\text{m}^2/\text{g}$  to 70–90  $\text{m}^2/\text{g}$ . The same trend can be seen when comparing the values of the electrochemical surface area (ECA) of the products. Generally, electrocatalysts with higher Pt-loadings yield thinner active catalyst layers in MEAs and electrodes, therefore they are gaining increased interest.

### 3.2. CO-tolerant anode catalysts

Practical operation of a PEMFC on a feed stream of reformat is necessary in order to demonstrate the utilization of this technology for widespread mobile application. Fuel feed streams based on reformat obtained by reforming of methanol or gasoline could result in somewhat inferior cell performance compared to the operation with pure hydrogen. After suitable CO removal techniques, such as water–gas shift and preferential oxidation (PrOx), a reformat gas contains about 40–100 ppm CO prior to entering the PEMFC anode. CO strongly chemisorbs onto the Pt surface at the operating potential of the anode, thereby poisoning the surface for  $\text{H}_2$  oxidation and degrading the cell performance. An improvement of CO-tolerance can be obtained with PtRu-systems [8], however, considerable efforts were necessary to meet the catalyst requirements for real operating PEMFC conditions.

A new anode electrocatalyst based on a carbon supported PtRu-bimetallic system was developed in the program. The product exhibits good CO tolerance up to concentrations of 100 ppm CO in the anode feed gas. A diagram showing the performance under various reformat/oxygen conditions is given in Fig. 3. With a simulated reformat gas mixture (60 vol.%  $\text{H}_2$ , 25 vol.%  $\text{CO}_2$ , 15 vol.%  $\text{N}_2$  and 100 ppm CO) and a low percentage of air bleed, the total cell voltage loss  $\Delta U_{\text{tot}}$  is about 50 mV at a current density of 1  $\text{A}/\text{cm}^2$  compared to operation under hydrogen. As the cell voltage loss  $\Delta U_{\text{CO}_2/\text{N}_2}$ , which is caused by dilution effects, sums up to about 30 mV, the resulting voltage loss of  $\Delta U_{\text{CO}} = 20$  mV can be attributed to CO poisoning. Characteristic data of the anode electrocatalyst are listed in Table 2.

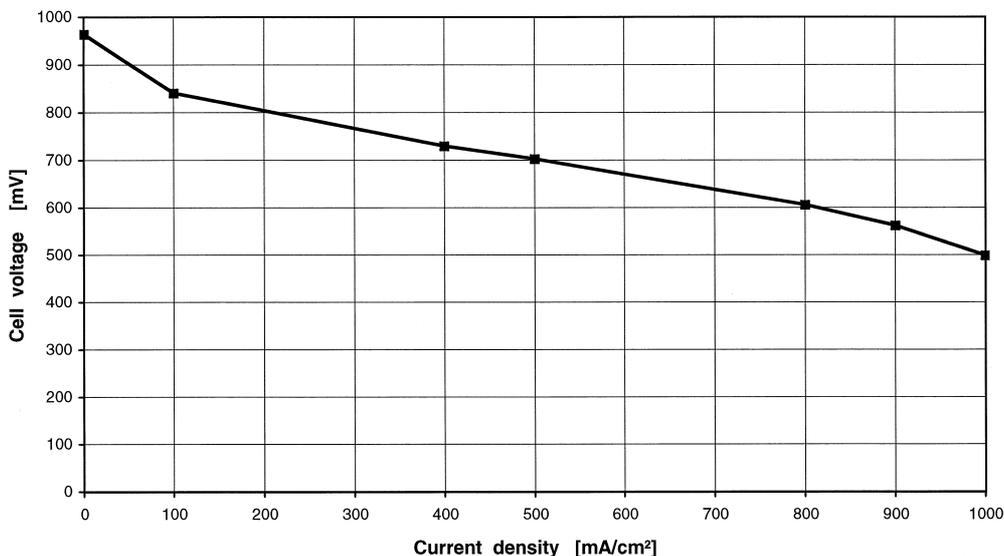


Fig. 4. Membrane-electrode-assembly (MEA); hydrogen/air operation (3/3  $\text{bar}_{\text{abs}}$ ). Anode/cathode-electrocatalyst: F 901KR/D 20% Pt, total Pt loading: 0.5 mg Pt/ $\text{cm}^2$ .  $T = 75^\circ\text{C}$ , active cell area 25  $\text{cm}^2$ .

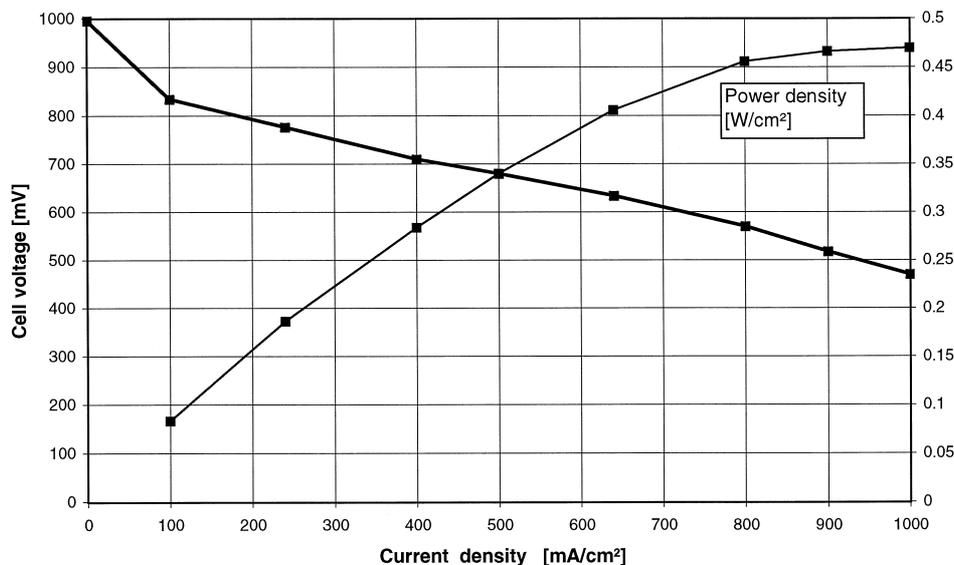


Fig. 5. Membrane-electrode-assembly (MEA); reformate/air operation (3/3 bar<sub>abs</sub>). Electroanalyst anode: FH901R/D, 20% PtRu, cathode: F901KR/D 20% Pt. Total Pt loading 0.5 mg Pt/cm<sup>2</sup>,  $T = 75^{\circ}\text{C}$ , active cell area 25 cm<sup>2</sup>.

Results of CO-stripping experiments and  $\Delta U/t$ -measurements under steady load conditions are in good correlation with the CO-tolerance data and were reported elsewhere [9].

### 3.3. Evaluation in PEMFC single cells and MEAs

The performance of the newly developed electrocatalysts was evaluated in PEMFC single cells with 25 cm<sup>2</sup> active cell areas on laboratory scale at Degussa-Hüls. Results of MEAs with low total Pt loadings (i.e., < 0.5 mg Pt/cm<sup>2</sup>) are shown in Figs. 4 and 5. Typically, power densities of up to 0.5 W/cm<sup>2</sup> at 1 A/cm<sup>2</sup> are obtained for

hydrogen/air as well as reformate/air conditions. Further details are given in the experimental section.

### 3.4. Electrocatalyst evaluation in PEMFC stacks

At the end of the program, the electrocatalyst materials were evaluated by DaimlerChrysler in a PEMFC short stack based on Ballard technology. Anode electrocatalyst FH901R/D, 20 wt.% PtRu and cathode electrocatalyst F901KR/D 20 wt.% Pt were used in this work.

The overall Pt loading was reduced to about 0.5 mg Pt/cm<sup>2</sup>. For hydrogen/air operation at a pressure of 3 bar<sub>abs</sub>, a peak power of 2.7 kW was obtained. The power density was > 0.4 W/cm<sup>2</sup> and exceeded the initial pro-

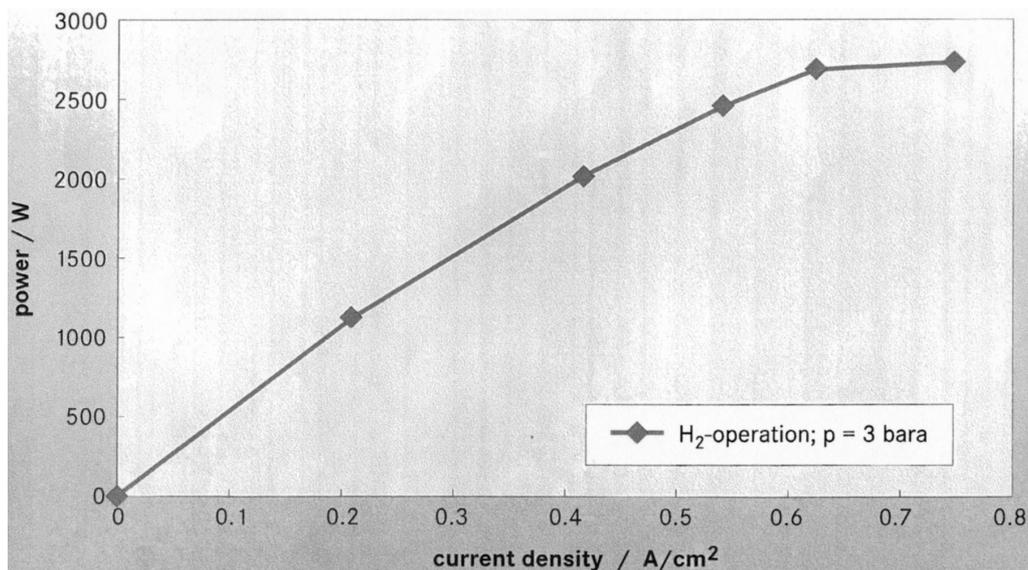


Fig. 6. Performance of BMBF low cost materials verified in a Ballard stack. Source: DaimlerChrysler.



Fig. 7. PEMFC demonstration stack. Source: DaimlerChrysler.

gram objectives. A power vs. current density diagram of the PEMFC stack is given in Fig. 6, a picture is shown in Fig. 7.

#### 4. Conclusion

Platinum-based electrocatalysts are playing an important role in the development of high performance PEMFC stacks for mobile applications. Cost reduction is a major task to be solved for the application of this technology in future vehicle propulsion systems.

The goal of this BMBF-funded research program was to develop the basic technology and components of PEMFC stacks for use in transport applications. In the framework of this project, Degussa-Hüls developed precious metal-based electrocatalysts for operation under hydrogen/air and reformat/air PEMFC conditions.

Considerable progress was made to reduce the overall platinum loading of PEMFC single cells and stacks. High power densities up to  $0.5 \text{ W/cm}^2$  at low total platinum loadings of less than  $0.5 \text{ mg Pt/cm}^2$  were achieved, thus exceeding the initial project targets. A CO-tolerant anode electrocatalyst, exhibiting a CO-tolerance of up to 100 ppm CO, was developed. The performance of the new electrocatalyst materials was verified by DaimlerChrysler in a PEMFC demonstration stack at the end of the program.

Development work is ongoing to further improve electrocatalysts and MEAs to meet the targets for widespread commercialization of PEMFC in electric vehicles.

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