# The PEMFC-integrated CO oxidation — a novel method of simplifying the fuel cell plant

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## Abstract

Natural gas and methanol are the most economical fuels for residential fuel cell power generators as well as for mobile PEM-fuel cells. However, they have to be reformed with steam into hydrogen, which is to be cleaned from CO by shift-reaction and by partial oxidation to a level of no more than 30 ppm CO. This level is set by the Pt/Ru–C-anode of the PEMFC. A higher partial oxidation reaction rate for CO than those of Pt/Ru–C can be achieved in an oxidic Au–catalyst system. In the $Fe_2O_3$–Au system, a reaction rate of $2 \cdot 10^{-3}$ mol CO/s g Au at 1000 ppm CO and 5% ''air bleed'' at 80°C is achieved. This high rate allows to construct a catalyst-sheet for each cell within a PEMFC-stack. Practical and theoretical current/voltage characteristics of PEMFCs with catalyst-sheet are presented at 1000 ppm CO in hydrogen with 5% ''air bleed''. This gives the possibility of simplifying the gas processor of the plant. © 1999 Elsevier Science S.A. All rights reserved.

## 1. Introduction

Compared with other types of fuel cells, PEM-fuel cells are most suitable for discontinuous operation and quick start up, if they are operated with pure hydrogen as the fuel gas. Operating the cell with natural gas or methanol, the operation conditions and the times for quick load changing are determined by the slower dynamic of the methanol- or $CH_4$-reformer and the reformer gas cleaning units. To avoid these disadvantages, we are developing a thin catalyst-sheet for PEMFC-integrated CO oxidation [1,2].

## 2. Experimental

At first, we prepare several oxidic Au–catalyst powders by co-precipitation and fill these powders into a Ni-foam-sheet by cold-pressing at 1 t/cm$^2$ [2]. Second, we determine the selective CO oxidation rate in $H_2$ plus 1% $O_2$ at 80°C in an external reactor for differential flow [4].

Third, we place the catalyst-sheet into a 25 cm$^2$ PEMFC in front of the Pt/Ru–C-anode — but separated by a carbon-paper, which separates the acidic electrode from the Ni-foam and provides the electric contact between the catalyst-sheet and the anode (Fig. 1).

## 3. Results and discussion

### 3.1. The rate of CO oxidation of several oxidic Au–catalysts

We are investigating the rate of the selective CO oxidation in $H_2$ at 1% CO content and 1% oxygen content at 80°C in an external differential flow reactor for Au/Fe$_2$O$_3$-catalysts with several structures (Table 1, catalyst numbers in relation to composition of the carrier-oxides Fe$_2$O$_3$/MeO).

The rates of the selective CO oxidation of the Au–catalysts at 80°C are higher than the rate of Pt/Al$_2$O$_3$-catalyst at 200°C. This is caused by the more weakly adsorbed CO on the Au-surface in relation to the adsorption on Pt-surface at low temperatures. The reaction rate of chemisorbed

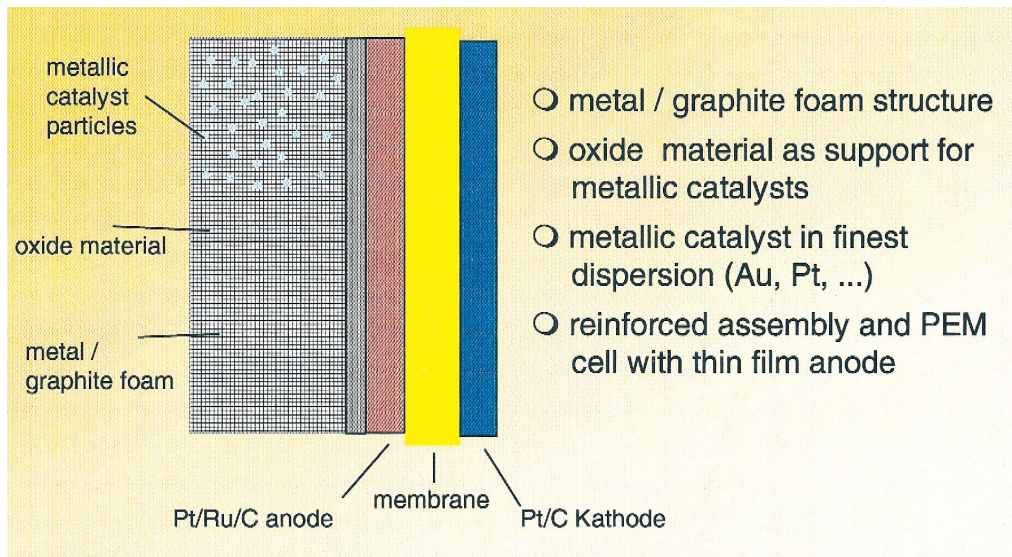* Corresponding author. Tel.: +49-7-31-95-30-207; fax: +49-7-31-95-30-666; E-mail: bernd.rohland@huba.zsw.uni-ulm.de

Fig. 1. PEMFC with catalyst-sheet.

oxygen with adsorbed CO is higher on the Au/Fe-interface than on the Pt/Al$_2$O$_3$-interface, because on Pt, the CO is too strongly bonded at low temperatures. Up to 180–200°C, the CO-bonding strength on Pt is comparable with the CO-bonding strength on Au at 80°C.

The decreasing of the rate with time (rate change in the third column of Table 1) is caused by the absence of water vapor and O$_2$ content in the fuel stream (e.g., synthetic methanol reformate). In a real fuel stream, this decrease does not take place. Here, the increase of weight by treatment of the catalyst with H$_2$/CO$_2$-mixture is stopped up to an oxygen content of 0.3%. This is mainly caused by blocking the surface-reaction of the reduced catalyst with CO$_2$ to form FeCO$_3$ by the dissociative chemisorbed oxygen.

### 3.2. The CO-tolerance of a PEMFC with and without catalyst-sheet

We investigated a 25 cm$^2$ PEMFC with Pt/Ru–C-anode (0.3 mg/cm$^2$ Pt/Ru) with and without catalyst-sheet (Figs. 2 and 3).

Table 1
Rate of CO oxidation in H$_2$ for several catalysts at 1% O$_2$ content at 80°C

| Catalyst number | Initial rate (mol/s g Au) | rate after 24 h of treatment (mol/s g Au) |
|---|---|---|
| Pt/Al$_2$O$_3$, 200°C | $1.9 \cdot 10^{-3}$ | $1.2 \cdot 10^{-3}$ |
| Au/100996, 80°C | $2.9 \cdot 10^{-3}$ | $1.8 \cdot 10^{-3}$ |
| Au/260598, 80°C | $3.0 \cdot 10^{-3}$ | $1.9 \cdot 10^{-3}$ |
| Au/280598, 80°C | $4.9 \cdot 10^{-3}$ | $3.2 \cdot 10^{-3}$ |
| Au/291097, 80°C | $5.1 \cdot 10^{-3}$ | $2.8 \cdot 10^{-3}$ |
| Au/061197, 80°C | $7.8 \cdot 10^{-3}$ | $5.2 \cdot 10^{-3}$ |

First, we determined the relation between voltage drop to pure H$_2$ at 900 mA/cm$^2$ under variation of the CO- and air contents of the PEMFC-anode *without* catalyst-sheet.

The PEMFC tolerates 100–150 ppm CO at 5% air content in H$_2$ and 50 ppm CO at 1% air content. Without air content in H$_2$, the PEMFC tolerates no more than 30 ppm CO.

As shown in Fig. 3 for CO-free H$_2$, there is no difference between the $U$–$i$-plot for pure H$_2$ *with* and *without* catalyst-sheet. This shows that the catalyst-sheet does not significantly hinder the gas transport to the anode or cause additional ohmic losses. At 750 ppm CO content in H$_2$ with 1% O$_2$ content, we obtain a significant improvement in the cell performance *with* catalyst-sheet compared to the performance *without* catalyst-sheet. The $U$–$i$-plot of the PEMFC *with* catalyst-sheet shows a little difference of 50–75 mV to pure H$_2$ at 200–900 mA/cm$^2$, whereas the $U$–$i$-plot of the same PEMFC *without* catalyst-sheet shows a difference of more than 700 mV up to the start of oscillations at 150 mA/cm$^2$ under equivalent conditions and only 500 ppm CO.

For the catalyst number 291097 inside the catalyst-sheet DA 103 (DA = double-layer anode; catalyst-sheet numbers = sheets with several composed catalysts) we have obtained 5000 ppm CO-conversion at 3% O$_2$, 3000 ppm CO-conversion at 2% O$_2$ and 1000 ppm CO at 1% O$_2$ in H$_2$ at 50 mV voltage drop to pure H$_2$ at 900 mA/cm$^2$.

From these data, we can determine the O$_2$-dependence of the rate of CO oxidation $r$(CO) of the applied catalyst number 291097 (if the catalyst is situated inside a Ni-foam and give catalyst-sheet DA 103). compared with the differential reactor determined O$_2$-dependence [3]:

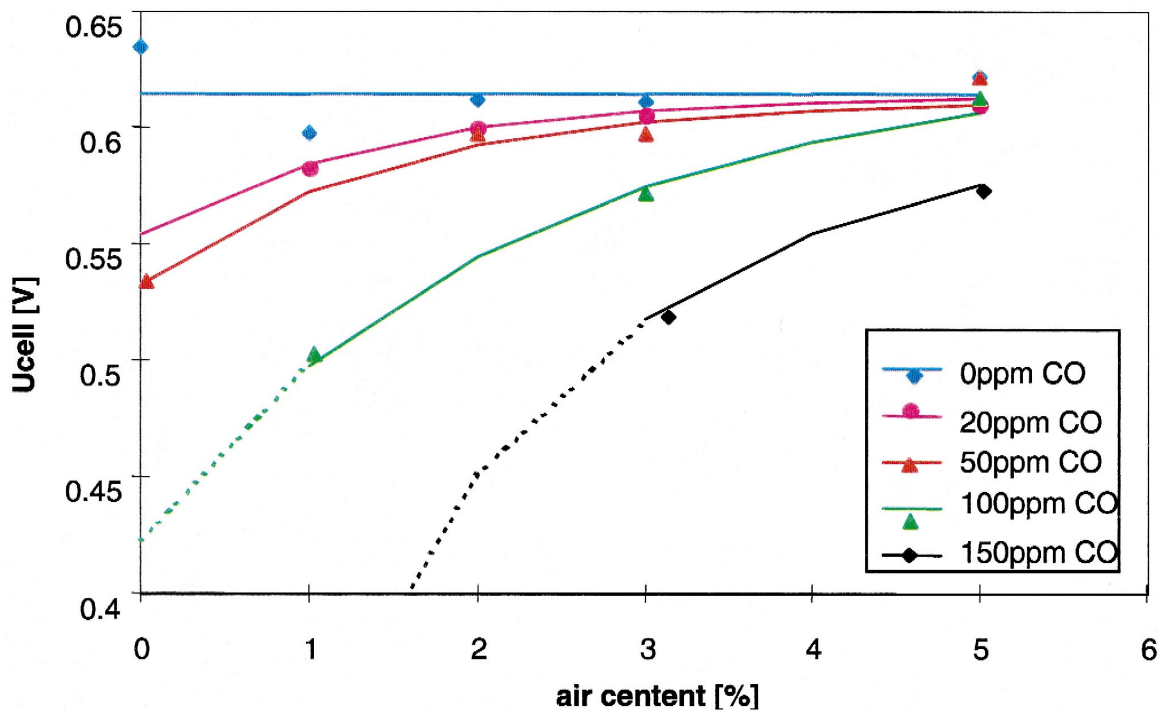$$r(\text{CO}) = r(1\% \text{ CO}, 1\% \text{ O}_2) \cdot x\text{CO}^{0.50} \cdot x\text{O}_2^{0.25} \qquad (1)$$

Fig. 2. Cell voltage of a PEMFC without catalyst-sheet in dependence of CO and air content in $H_2$ at 900 mA/$cm^2$, $T = 70°C$.
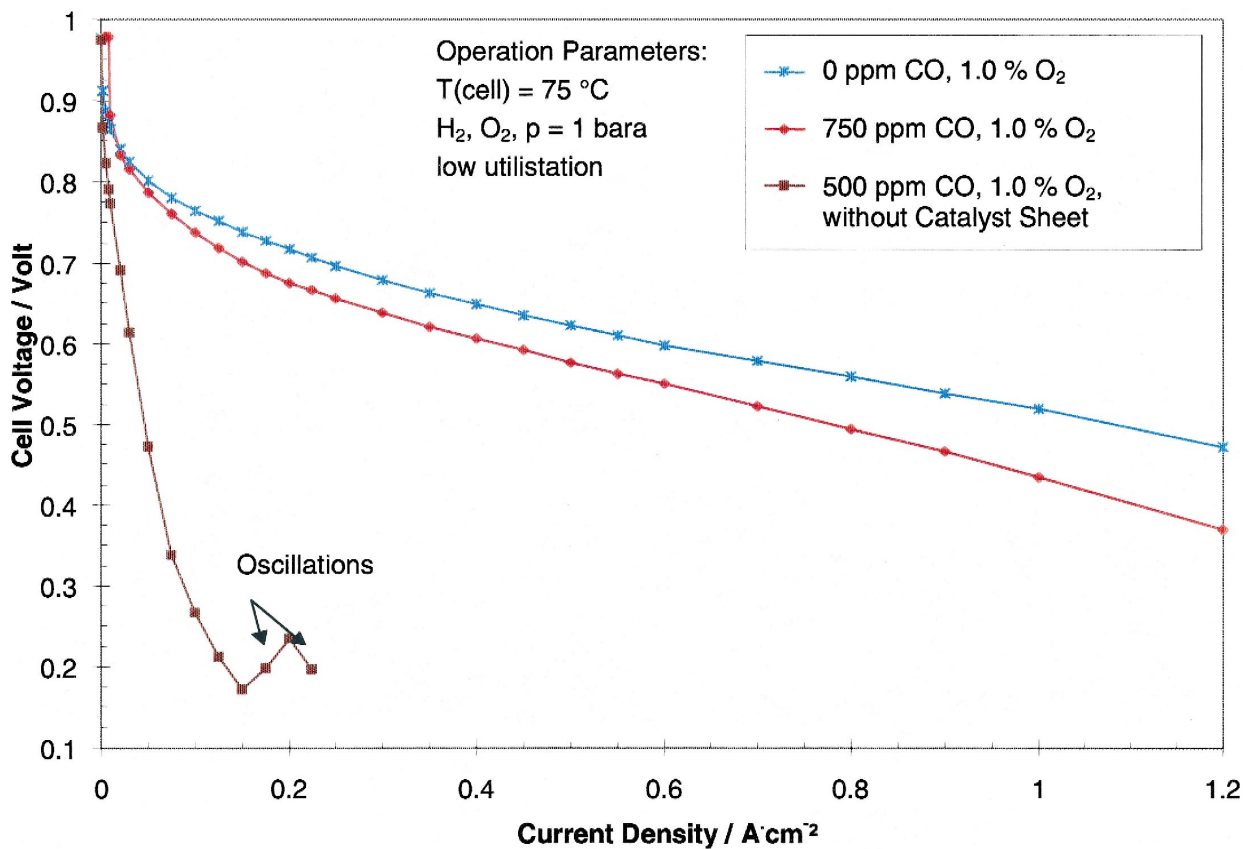


Fig. 3. $U–i$-plots of PEMFC with and without catalyst-sheet DA 103 operation with CO-containing $H_2$.

we obtain a higher exponent for $O_2$-dependence at higher $O_2$ content:

$$r(CO, catalyst - sheet) = r(1\% O_2) \cdot xO_2^{1.5} \qquad (2)$$

This is caused by the additional dependence of the overvoltage of the Pt/Ru-anode on the oxygen content in the $H_2$, which is outcoming from the catalyst-sheet at 900 mA/$cm^2$ (Fig. 2), if PEMFC is operating under the conditions listed in Table 2.

### 3.3. The rate of selective CO oxidation inside the catalyst-sheet

Oxide-supported Au–catalysts have a wide spread rate and selectivity of CO oxidation in $H_2$. The rate $r(CO)$ depends on the effective spill-over between CO-adsorption on Au–catalyst particles and the oxygen-adsorption on the oxide surface near the circumference-line of the Au–catalyst. At small Au–catalyst particles with a size of 2–4 nm, the state of adsorbed oxygen plays the main role. Highest rates occur, if oxides guarantee a dissociative oxygen adsorption. This takes place on iron-oxides and related metal oxides. In this case, the spill-over effect is amplified by water vapor, which gives very reactive OH-species on the oxide surface. Without water vapor, the rate of selective CO oxidation goes slowly (column 3 of Table 1).

The CO-conversion $X(CO)$ inside the catalyst-sheet depends mainly on the current density. This is caused by the dependence of the CO-stream to the Pt/Ru-anode on the molar Faradaic $H_2$-stream $\dot{v}_m (H_2)$ and the CO content, $x(CO)$, in $H_2$:

$$X(CO) = r(CO)/\dot{v}_m(H_2) \cdot x(CO)_{in} \qquad (3)$$

Table 2
CO-limits for 50 mV voltage drop to pure $H_2$ at 900 mA/$cm^2$, temperature- and $pO_2$-dependence

| Catalyst-sheet temperature | ppm CO 3% $O_2$ | ppm CO 2% $O_2$ | ppm CO 1% $O_2$ | ppm CO 0.5% $O_2$ |
|---|---|---|---|---|
| DA 007 75°C | 3000 | 1000 | 250 | – |
| DA 009 75°C | 5000 | 1800 | 500 | – |
| DA 101 75°C | 2000 | 1100 | 500 | – |
| DA 103 75°C | 5000 | 3000 | 1000 | 300 |
| DA 103 60°C | 2000 | 1300 | 650 | – |
| DA 103 45°C | 900 | 600 | 450 | – |

Table 3

| $x(CO)$, limit in ppm | 900 | 1800 | 4500 |
|---|---|---|---|
| $i$ (A/$cm^2$) | 1.0 | 0.5 | 0.2 |

Then the integral rate of the selective CO oxidation in $H_2$ at constant CO-conversion of 95% is given by:

$$r(CO) = 0.95 \cdot \dot{v}_m(H_2) \cdot x(CO)_{in} \qquad (4)$$

From this, we obtain the following results of CO-limits in the inlet $H_2$-gas for 95% CO-conversion according to 50 mV voltage drop to pure $H_2$ for the catalyst-sheet number DA 103 at 1% $O_2$ content (Table 3).

## 4. Conclusions

If we can treat a PEMFC-stack *with* catalyst-sheet in front of the Pt/Ru-anode of each cell, we need only to lower the CO content by an external CO-cleaning device to 1000–2000 ppm CO. That means, we can eliminate the second stage of the external reactor for the reformer-off-gas. The advantage is a better dynamic and a simpler construction of the $H_2$-producing unit of the PEMFC-plant.

## Acknowledgements

## References

[1] B. Rohland, et. al., Integraler PEM-Brennstoffzellen-Heizungsmodul sowie Brennstoffzellen-Stapel, Patent DE 197 18 970.9.
[2] V. Plzak, B. Rohland, Zusammenhang zwischen Aktivität und Stabilität von Katalysatoren zur selektiven Niedertemperatur — CO oxidation in Reformergas, Proc. XXXI Jahrestreffen deutscher Katalytiker, S. 213, Leipzig, 1998.
[3] M. Kahlich et al., J. Catal (in press).
[4] H.A. Gasteiger et al., Selective CO oxidation: from model to reality,