

## Gold-Composite Electrodes for Hydrocarbon Sensors Based on YSZ Solid Electrolyte

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**Abstract.** In potentiometric zirconia based sensors gold electrodes show a high sensitivity for hydrocarbons (HC's) when the measurements are carried out in non equilibrated oxygen containing gas mixtures at temperatures < 700 °C. This behaviour explained by mixed potential theory is not stable and depends strongly on preparation and particularly on measuring conditions. To modify the electrode behaviour composites consisting of gold and gallium oxide were investigated. Gold pastes with different amount of Ga<sub>2</sub>O<sub>3</sub> were prepared and screen printed on YSZ pellets. After sintering at defined temperatures between 900 and 950 °C the cells were tested regarding the electrode behaviour in a C<sub>3</sub>H<sub>6</sub>, O<sub>2</sub> gas mixture using a platinum air reference electrode. These composite electrodes show as compared with pure gold an enhanced sensitivity at low propylene concentrations and a time-independent characteristic at high concentrations of C<sub>3</sub>H<sub>6</sub>. The optimal composition is found to be at 20 mass-% Ga<sub>2</sub>O<sub>3</sub>. This electrode can be treated in reducing gases at temperatures 850 °C without changing its characteristics.

### 1. Introduction

Mixed potential electrochemical sensors based on yttria stabilised zirconia (YSZ) solid electrolyte are suited for the "in-situ-measurement" of combustible components in exhaust gases. Components such as CO or hydrocarbons (HC's) have to be monitored in order to control the industrial combustion processes and the catalytically exhaust gas combustion of automotive engines for the "on-board-diagnosis". A mixed potential sensor combines an equilibrium or oxygen electrode and a second electrode which shows a low oxygen sensitivity but a high hydrocarbon sensitivity. Both electrodes may be exposed to the analyte gas. Alternatively, the sensor can be operated with an oxygen electrode which uses air as an external reference [1].

Up to now a number of materials have been investigated as hydrocarbon sensitive electrode material for

solid electrolyte sensors, for instance gold, gold alloys, mixed oxides like rare earth chromites [2,3] and Tb doped YSZ [4]. The following problems occurred: low temperature stability (Au), time-dependent results (Au, chromite), high electrode resistances (chromite), low HC-sensitivity (chromite).

It is well known that gold is a very promising material for desired electrodes because of its low catalytic activity for the combustion of gaseous hydrocarbons. But the value of its potential demotes probably due to the coarsening of gold particles. Furthermore, layered structures based on a combination of gold and oxides such as TiO<sub>2</sub> [1] and Nb<sub>2</sub>O<sub>5</sub> [2] have also been investigated. But such electrodes showed more or less equilibrium behaviour that means their catalytic activity for the chemical combustion of hydrocarbons is too high.

In order to stabilize the gold electrode in its mor-

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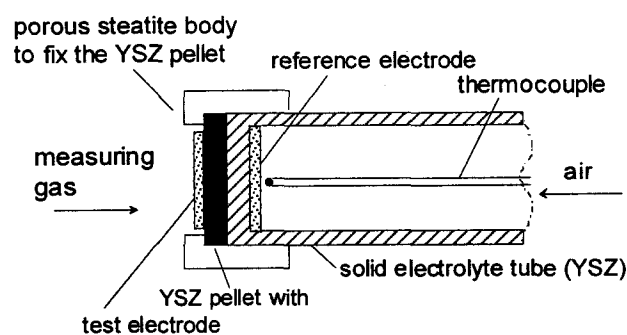


Fig. 1. Cell arrangement (schematic).

phology and to modify the catalytic activity we investigated gold-oxide composites. Gallium oxide seems to be a good candidate because it is well known as catalytically inactive material for the combustion of HC's [5].

## 2. Experimental Description

The starting materials for the electrodes were pure gold powders and its mixtures with 20, 30 and 40 mass-%  $\text{Ga}_2\text{O}_3$ -powders from which pastes for screen printing (Heraeus GmbH, Hanau, Germany) were produced. The pastes of  $5 \text{ cm}^2$  were printed squarely 5 times on YSZ solid electrolyte pellets of 12 mm in diameter and 2 mm in thickness. The samples which were sintered at temperatures of  $900 \text{ }^\circ\text{C}$ ,  $930 \text{ }^\circ\text{C}$  and  $950 \text{ }^\circ\text{C}$  exhibited electrode layers of approximately  $10 \text{ }\mu\text{m}$  thickness. As an example for understanding: Au30Ga denotes gold with 30 mass-% gallium oxide.

Figure 1 illustrates the cell arrangement for the measurement of the propylene characteristic of the samples. The YSZ pellet with the electrode to be investigated was pressed onto the closed end of a zirconia tube. The air reference electrode in the inner side of the zirconia tube was made of platinum. The cell voltages were measured between the both electrodes by means of a computer controlled digital multimeter (Keithley 199). The test equipment and the test procedures are described in more detail elsewhere [1].

For all investigations we used a carrier gas of nitrogen containing 1.5 vol.-% oxygen. In all cases the flux was 200 ml/min and the measuring temperature  $700 \text{ }^\circ\text{C}$ . The propylene content increases from 0 to 0.8 vol.-% in the following steps: 0, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7 and 0.8. The propylene concentration in the gas was kept constantly for 10 minutes.

## 3. Theoretical Considerations

Depending on their catalytic activity of the used electrode materials the electrodes behave differently in non equilibrated gas mixtures.

On the surface of an electrode with high catalytic activity, the combustible components are oxidized, the gas is equilibrated in its vicinity and the equilibrium electrode potential is established. This electrode shows a Nernstian behaviour. For a test gas with hydrocarbon  $\text{C}_m\text{H}_n$  and an excess of oxygen, the cell voltage follows the equation [3],

$$U = \frac{RT}{4F} \ln \left[ \frac{p(\text{O}_2) - (m + n/4)p(\text{C}_m\text{H}_n)}{p(\text{O}_2)_{\text{ref}(\text{air})}} \right] \quad (1)$$

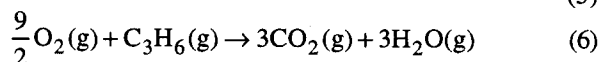
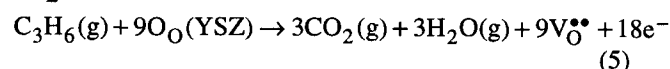
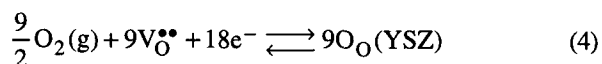
In the case of an excess of combustibles, e.g. of propylene the cell voltage depends on the equilibrium gas composition:

$$U = \frac{RT}{4F} \ln \left[ \left( \frac{p(\text{CO}_2)^3 p(\text{H}_2\text{O})^3}{K_{p,T} p(\text{C}_3\text{H}_6)} \right)^{2/9} / p(\text{O}_2)_{\text{air}} \right] \quad (2)$$

where  $K_{p,T}$  is the temperature-dependent constant of the mass action law.

$$K_{p,T} = \frac{p(\text{CO}_2)^3 p(\text{H}_2\text{O})^3}{p(\text{O}_2)^{9/2} p(\text{C}_3\text{H}_6)} = f(T) \quad (3)$$

When we have an electrode with low catalytic activity for the conversion of combustible components, so these are incompletely oxidized on the electrode. The potential should be determined by the following two competing electrode processes, i.e., the oxygen electrode (4) and the hydrocarbon electrode (5):



The cell voltage obtained in the non equilibrated gas mixture does not follow the Nernstian equation provided that the temperature is low ( $< 700 \text{ }^\circ\text{C}$ ). From the theory of mixed potential the voltage is established according to the kinetics of the summary of electrode reactions (4) and (5). The measure of the kinetics is the exchange current

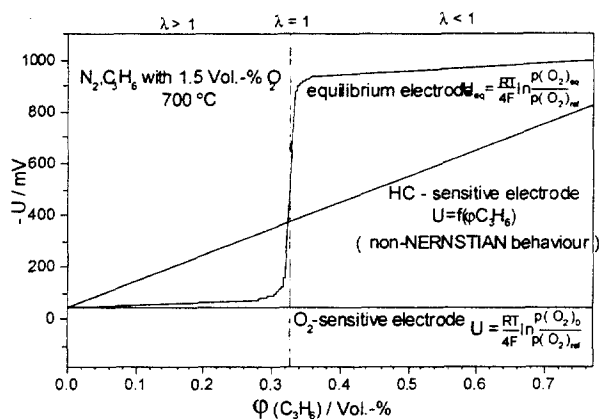


Fig. 2. Propylene characteristic of three idealized electrodes

density of these reactions [8]. More qualitatively speaking, if the electrode reaction (5) is faster than the oxygen electrode reaction (4) the electrode potential is mainly affected by the  $C_3H_6$  concentration. The electrode shows an HC-sensitivity and the electrode potential a so called non-Nernst behaviour.

Figure 2 shows schematically the cell voltage of the galvanic solid electrolyte cells with an air electrode and three idealized measuring electrodes in dependence on the propylene content in a test gas. The voltage curve of a cell with an equilibrium electrode is characterized by the well known  $\lambda$ -leap. The test gas equilibrates on the electrode surface. The cell voltages show the Nernst behaviour and follows the eq. (1) in the region of an excess of oxygen (lean mixtures) and the eq. (2) (rich mixtures) after the leap in the excess of hydrocarbon. An idealized oxygen electrode should be completely inactive for all chemical reactions. The cell voltage depends on the free oxygen in the test gas only. In Fig. 2 the graph is in parallel with the concentration axis. The behaviour of an ideal hydrocarbon electrode can be described as follows: The test gas does not equilibrate at the electrode; the cell voltage depends only on the hydrocarbon content. But in the real case, the oxygen content has a more or less influence on the electrode reactions. So a mixed potential results and the voltage curve depends on the oxygen concentration, as well.

#### 4. Results and Discussion

The following selection procedure was realized to find the electrode with the highest HC- sensitivity among the three Au-Ga<sub>2</sub>O<sub>3</sub>-mixtures (Au20Ga, Au30Ga, Au40Ga) and pure gold, sintered at three temperatures on the YSZ

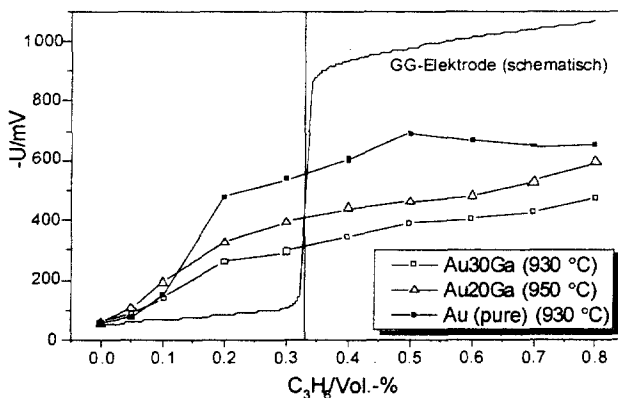


Fig. 3. Propylene characteristic of Au20Ga (950 °C) and Au30Ga (930 °C) after tempering at 800 °C and Au (pure, 930 °C).

solid electrolyte: The first measurement was a scan, in which the propylene content gas was increased in the test from 0 up to 0.8 Vol.-%. According to this measurement Au40Ga behaves like an equilibrium electrode. After the second measurement, a scan step by step up to highly reducible atmosphere and going down to oxidizing conditions was performed. Three samples were useable in respect of potential stability (Au20Ga, sintered at 950 °C; Au30Ga, sintered at 930 °C; Au30Ga, sintered at 950 °C). The other electrodes showed the same time-dependent behaviour as pure gold. The third measurement was a stress test: the samples have been cooled down in a strongly reducing atmosphere. After this a normal scan followed. Two kinds of electrodes, the Au20Ga (sintered at 950 °C) and the Au30Ga (sintered at 930 °C) on the solid electrolyte seem to be optimal with regard to the sensitivity and the potential stability. In Fig. 3 the propylene characteristic of both electrodes is shown. For comparison the characteristic of an equilibrium electrode and of pure gold electrode were included in the figure. At lower  $C_3H_6$  concentration the sensitivity of the gold electrode is lower compared to the above mentioned Au/Ga compositions. At higher  $C_3H_6$  concentrations the sensitivity is indeed higher but the values are not stable and the slope of the curve is negative in some parts.

After tempering at 800 °C for one week and an additional tempering at 850 °C for one week the hydrocarbon sensitivity of the two electrodes was well preserved. In Fig. 4 the comparison of the two electrodes regarding the propylene characteristic after the temperings is presented. The Au20Ga-electrode, sintered at 950 °C on YSZ shows

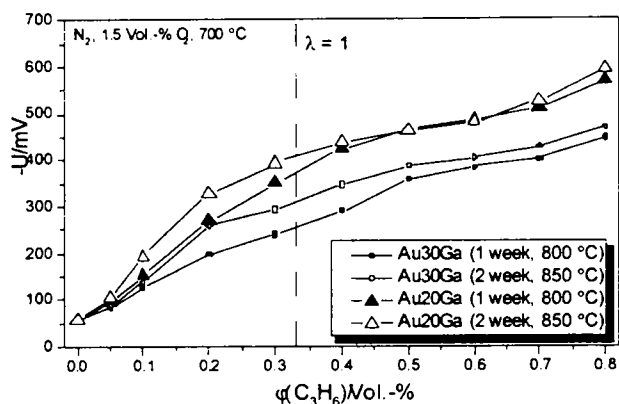


Fig. 4. Propylene characteristic of Au20Ga (950 °C) and Au30Ga (930 °C) after tempering at 800 °C and 850 °C.

among the electrodes investigated the highest C<sub>3</sub>H<sub>6</sub>-sensitivity.

The propylene characteristic of both electrodes in comparison with an other hydrocarbon sensitive electrodes is shown in Fig. 5. The C<sub>3</sub>H<sub>6</sub>-sensitivity of the special substoichiometric gallium doped lanthanum chromite electrode [3] is considerable lower. It should be noted that the values of cell voltages are dependent on flow rate and therefore only suitable for comparison of different electrodes. At low flow rates which correspond to long time of residence electrodes tend to achieve the equilibrium behaviour because of the chemical reaction of HC's with oxygen.

The increase of the potential curves of the two Au-Ga<sub>2</sub>O<sub>3</sub>-electrodes is high enough for their application in an HC-sensor based on YSZ solid electrolyte.

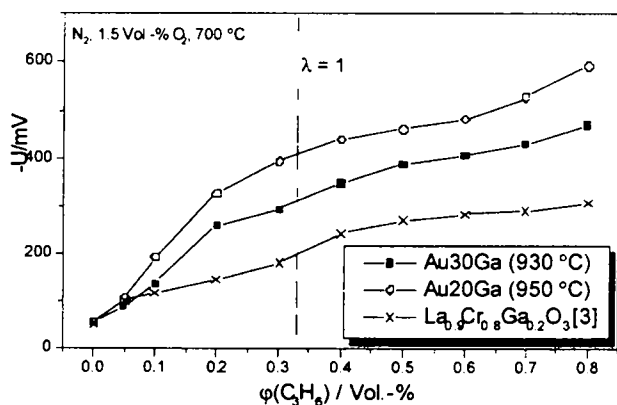


Fig. 5. Propylene characteristic of Au20Ga (950 °C), Au30Ga (930 °C) and La<sub>0.9</sub>Cr<sub>0.8</sub>Ga<sub>0.2</sub>O<sub>3</sub> [3].

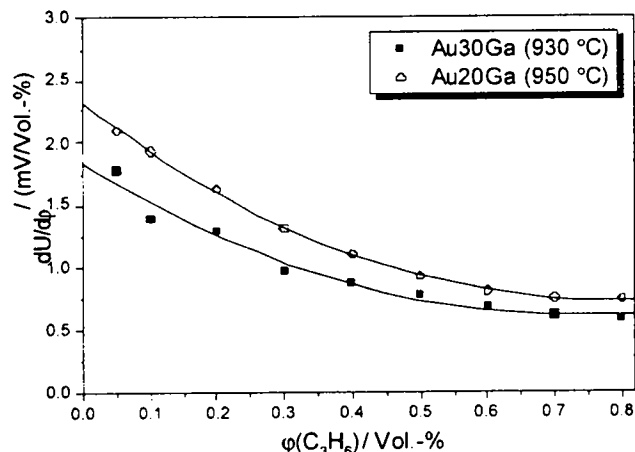


Fig. 6. Sensitivity of Au20Ga (950 °C) and Au30Ga (930 °C).

The sensitivity of the two electrodes is presented in Fig. 6. The cell voltage measured in the 1000 vol.-ppm propylene test gas vs. air is about 200 mV for the electrode consisting of Gold with 20 mass-% gallium oxide, sintered at 950 °C. For small concentrations of propylene the sensitivity, that means the ratio of the voltage and the propylene concentration is higher than for the propylene rich area. Therefore, these electrodes should be useable especially for the detection of small amounts of hydrocarbons in oxidising atmosphere.

#### 4. Conclusions

Composites consisting of gold-gallium oxide mixtures are suitable as an electrode material for potentiometric hydrocarbon sensors because of their high C<sub>3</sub>H<sub>6</sub>-sensitivity and stable electrode potentials in gases with hydrocarbons. The behaviour of the electrodes depends strongly on the ratio of gold/gallium oxide and the sintering temperature for the electrode layers. Gold with 20 mass-% gallium oxide, sintered at 950 °C seems to be the optimal one with respect to the sensitivity and the potential stability.

#### 5. References

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