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# Electrochemical investigations on multi-metallic electrodes for amperometric NO gas sensors

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## Abstract

The activities of Pt/YSZ, PtAu/YSZ and RhPtAu/YSZ thick film electrodes in $O_2$, $N_2$ and NO, $N_2$ gas mixtures at high temperatures were investigated by electrochemical impedance spectroscopy (EIS) and linear sweep voltammetry (LSV). As compared with the Pt/YSZ electrode the cathodic $O_2$ reduction at both multi-metallic electrodes is strongly inhibited, which is confirmed by charge transfer resistance for cathodic $O_2$ reduction as follows: $R_{ct}(Pt/YSZ) < R_{ct}(PtAu/YSZ) < R_{ct}(RhPtAu/YSZ)$. In contrast to that the cathodic NO reduction is accelerated only by the RhPtAu/YSZ electrode, indicating that the RhPtAu mixture is a suitable working electrode material for amperometric NO sensors based on the solid electrolyte (YSZ). A new amperometric NO sensor with only one working electrode made of RhPtAu mixture was tested in simulated gas mixtures containing NO, $O_2$, $N_2$, resulting in a linear response to the NO concentration, which is nearly independent of the $O_2$ concentration.
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## 1. Introduction

For in situ monitoring of NO in exhaust gases of lean burn engines amperometric NO gas sensors based on yttria stabilised zirconia (YSZ) can be used [1]. The development of these sensors is faced with the general problem of the cross-sensitivity of the NO sensitive electrode towards oxygen. Therefore amperometric NO gas sensors usually contain at least two working electrodes: the oxygen pumping electrode (OPE) and the NO detection electrode (NODE) where the NO concentration is measured in an essentially oxygen free gas mixture [1,2]. For oxygen pumping from the sensor Pt/YSZ electrodes are mainly applied due to their high catalytic activity for the $O_2$ reduction [3]. The NO cross-sensitivity of the OPE can be suppressed by modifying the Pt/YSZ electrode with additional metals or metal oxides [4,5]. Alter-

natively, it is possible to design sensors without OPE, if NODEs with negligible $O_2$ sensitivity and high NO sensitivity are available. For this purpose multi-metallic PtAu/YSZ and RhPtAu/YSZ electrodes were studied and compared with the Pt/YSZ electrode, employing electrochemical impedance spectroscopy (EIS) and linear sweep voltammetry (LSV).

## 2. Experimental

### 2.1. Preparation of the cells and NO sensors

Three types of solid state electrolyte cells, Pt/YSZ/Pt, PtAu/YSZ/Pt and RhPtAu/YSZ/Pt were prepared by thick film technology for testing the working electrode material (Fig. 1). Originally a metallic mixture of 10 wt.% Au and 90 wt.% Pt was chosen to decrease the NO activity of the Pt/YSZ electrode. Since the decrease of the $O_2$ activity of this AuPt/YSZ electrode was higher than the one
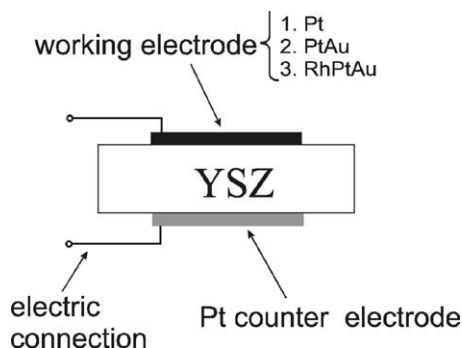
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Fig. 1. Schematic illustration of the electrochemical electrode test cell for EIS and LSV measurements.

of NO, the Pt component was "diluted" down to 10 wt.% Pt in order to get now a PtAu/YSZ electrode with very low $O_2$ activity in comparison with the Pt/YSZ electrode. Because the NO activity was also strongly diminished Rh was added to the PtAu(10/90)/YSZ electrode yielding RhPtAu($x$/10/90 − $x$)/YSZ, where $x$ amounted 5, 10, 20, 30 and 40 wt.% Rh, respectively. It turns out that for $x$ = 10 wt.% Rh the NO gas sensor performance was optimum. The Rh additive increased the NO activity of the PtAu(10/90)/YSZ electrode without increasing of the $O_2$ activity. Rh was chosen due to its high catalytic effect on the NO dissociation. It was also possible to use Rh(10)Au(90)/YSZ electrodes in the sensor, but the NO sensitivity was relatively low (about 0.6 nA/ppm NO).

Hence, for further studies cells were prepared in which Pt, PtAu(10/90) and RhPtAu(10/10/80) served as working electrodes (WE, 0.36 cm$^2$), made by mixtures of Pt paste (Heraeus), Au paste (Heraeus) and Rh powder (Aesar). In all of the three cells Pt/YSZ counter electrodes (CE) (0.36 cm$^2$) were used. YSZ ceramic sheets with the thickness 0.3 mm (Ceram Tec) served as substrate as well as solid state electrolyte for the cells.

The planar NO gas sensors with interdigitated electrodes were also prepared by thick film technology. The working electrode and the counter electrode of the sensor consisted of the same material (RhPtAu) and were screen printed onto one side of the YSZ substrate and finally sintered at 1000 °C for 1 h (Fig. 2) [6]. It is assumed that during the sintering
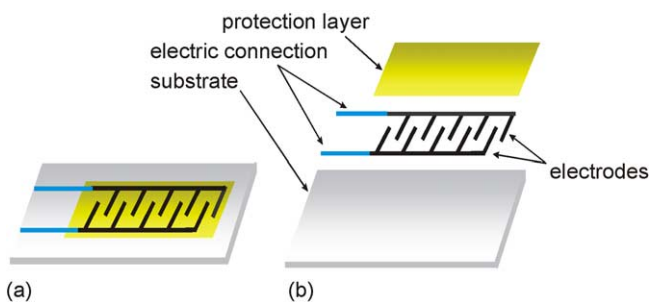


Fig. 2. Schematic illustration of the amperometric NO gas sensor design: (a) complete sensor; (b) sensor components.

process Rh and Pt atoms are distributed on the Au surface by grain boundary diffusion. The Rh atoms act as catalytic sites for NO dissociation.

The electrodes were covered with a glassy protecting layer to protect them from impurities in the gas.

### 2.2. Equipments and measurements

The cell under study was positioned in a quartz tube that was heated with a temperature controlled electric furnace (Carbolite).

In order to choose suitable working electrode material for amperometric NO gas sensors the EIS and LSV measurements were carried out at first on the electrochemical test cells (Fig. 1) in binary $O_2$, $N_2$ and NO, $N_2$ gas mixtures, respectively, at 550 and 600 °C. Then an amperometric NO sensor with only one working electrode made of RhPtAu/YSZ (Fig. 2) was tested at a constant potential of −400 mV in the ternary NO, $O_2$, $N_2$ gas mixtures simulating *typical* NO, $O_2$, $N_2$ concentration patterns that are typically for exhaust gases of diesel engines. The patterns depend on the engine operating mode (torque and speed). With decreasing $O_2$ content in the exhaust gas the possible NO concentration intervals shift to higher concentration values. The $O_2$ concentration in the gas mixtures ranged from 19 down to 6 vol.% and the NO concentration from 200 up to 1200 ppm. The gas flow rate was 100 ml/min.

The gas mixtures were prepared by an automatically working gas mixture apparatus (GO Meßtechnik, Greifswald). The mass flow rates of the individual gases as well as concentration patterns of the gas mixtures were regulated and controlled by the gas mixture apparatus via special dosage programs. A thermocouple close to the sensor serves as temperature controller. The thermovoltage was monitored by a digital voltmeter (RFT 1006500).

The impedance spectra were recorded by a commercial impedance spectrum analyser (IM5d, Zahner) in the frequency range from 0.1 Hz up to 1 MHz. A potentiostat (GPO3, Zirox Greifswald) controlled by a computer was used for quasi-stationary LSV measurements at a sweep rate of 0.5 mV s$^{-1}$ in the cathodic electrode potential range from 0 to −1 V. The potential of the working electrode was measured versus Pt-counter electrode which is considered to be an ideal reversible electrode.

## 3. Results and discussion

### 3.1. Studies of electrode materials

The Nyquist plots of the impedance spectra of the test cells, obtained from EIS measurements, show two semicircular arcs (Fig. 3). They can be interpreted by an equivalent circuit having two RC elements: $R_{se}C_{se}$ and $R_{ct}C_{dl}$ in series with a resistance $R_s$. Here $R_s$ sums up all resistances caused by electric connection and by impedances at high frequencies
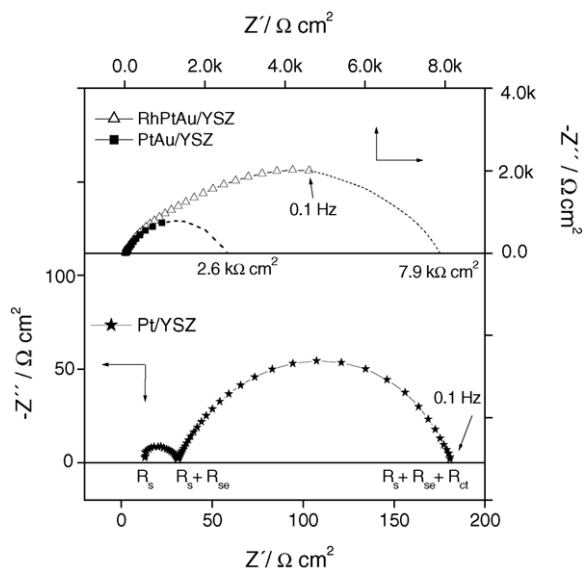
Fig. 3. Electrochemical impedance spectra for three different electrodes exposed to the $O_2$, $N_2$ gas mixture containing 1 vol.% $O_2$ at 600 °C, $U = 0$ mV.

$f > 1$ MHz, which cannot be resolved in detail due to the limitation of the measurement equipment. The $R_{se}C_{se}$ element corresponds to resistance and capacitance of the solid state electrolyte, respectively. They are almost equal for the three types of electrodes and do not depend on $O_2$ concentration or NO concentration. The $R_{ct}C_{dl}$ element represents charge transfer resistance and capacitance of the double layer, respectively. They depend not only on the $O_2$ concentration but also on the NO concentration. The charge transfer resistance increases proportionally to the reciprocal exchange current density $j_0$ ($R_{ct} \propto 1/j_0$), and therefore serves as a measure of the electrode reaction rate or electrochemical activity of the electrode. From EIS measurements the following order can be established:

$$R_{ct}(\text{Pt/YSZ}) < R_{ct}(\text{PtAu/YSZ}) < R_{ct}(\text{RhPtAu/YSZ}) \quad (1)$$

for cathodic $O_2$ reduction (Fig. 3). Obviously the addition of Au and Rh to Pt as working electrode generates an inhibitor effect on the $O_2$ reduction. It is known that for the Au/YSZ electrode $O_2$ chemisorption and exchange current density are lower than for the Pt/YSZ electrode [7]. The additional inhibition of the $O_2$ reduction by mixing Rh powder into the PtAu paste may be caused by partial oxidation of Rh.

The inhibitor effect is also confirmed by $j$–$U$ curves, given in Fig. 4, with the order of current densities:

$$|j_{O_2}(\text{Pt/YSZ})| > |j_{O_2}(\text{PtAu/YSZ})| > |j_{O_2}(\text{RhPtAu/YSZ})| \quad (2)$$

for the potential region $0 > U > -200$ mV.

The LSV measurements were performed at the RhPtAu/YSZ electrodes in binary $O_2$, $N_2$ and NO, $N_2$ gas mixtures, respectively. The obtained linear sweep voltammograms (LSVG) show one reduction step for $O_2$, $N_2$ gas mixtures but *two* reduction steps for NO, $N_2$ gas mixtures. The
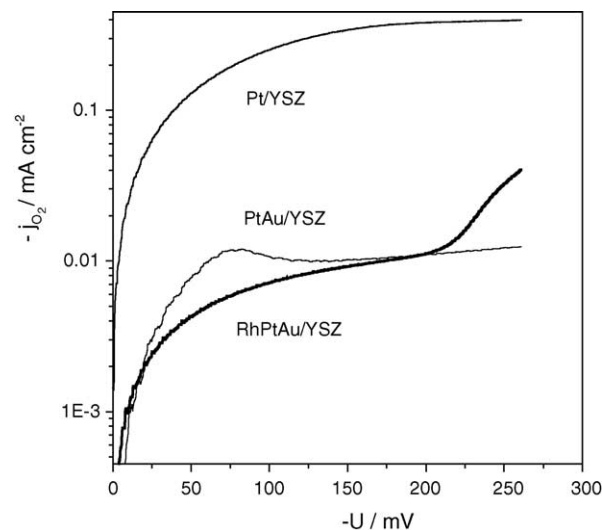


Fig. 4. $j$–$U$ curves for the three different electrodes exposed to 1 vol.% $O_2$, $N_2$ gas mixture at 600 °C.

steps appear as peaks in the derivative LSVG (Fig. 5). The first peak is attributed to the NO reduction and the second one to the $O_2$ reduction, respectively. No peak appears at potentials between $-250 < U < 0$ mV in $O_2$, $N_2$ gas mixtures and $dj/dU$ converges to zero, e.g. $R_p$ tends to infinity because $dj/dU$ corresponds to the reciprocal of the polarisation resistance $R_p$. This means that in this potential range the RhPtAu/YSZ electrode is polarisable for $O_2$ reduction. In contrast to that behaviour the RhPtAu/YSZ electrode is very active for NO reduction confirmed by the sharp peak at about $-180$ mV in the NO, $N_2$ gas mixture. Hence RhPtAu/YSZ meets the requirements of a NO detection electrode for the amperometric NO sensor with no or very low $O_2$ sensitivity and high NO sensitivity.
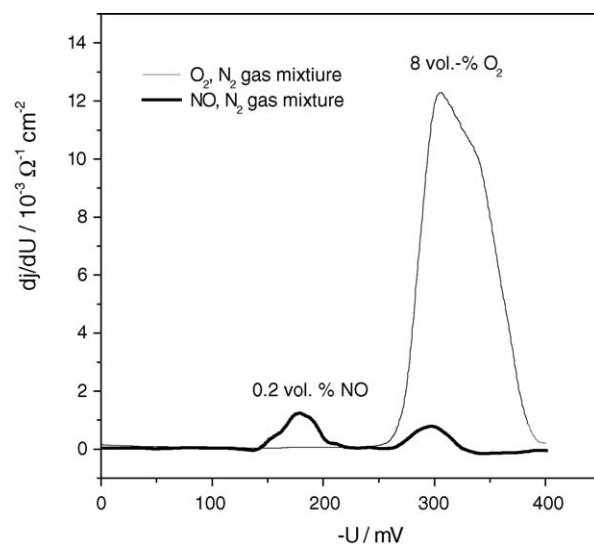


Fig. 5. Derivative linear sweep voltammograms of the RhPtAu/YSZ electrode exposed to 8 vol.% $O_2$, $N_2$ and 0.2 vol.% NO, $N_2$ gas mixtures, respectively, at 550 °C.
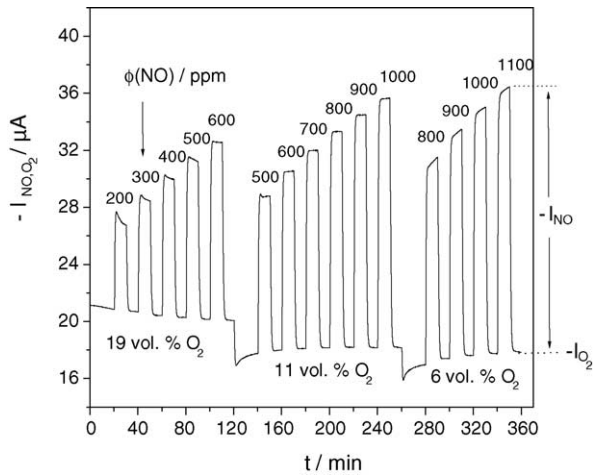
Fig. 6. Current response of the amperometric NO gas sensor with RhPtAu/YSZ metallic mixture electrodes exposed to NO, O$_2$, N$_2$ gas mixtures at 600 °C and −400 mV.

## 3.2. Test of the amperometric NO gas sensors

A series of amperometric NO gas sensors of the type RhPtAu/YSZ/PtRhAu (Fig. 2) was systematically tested in ternary gas mixtures with simulated NO, O$_2$, N$_2$ concentration patterns at the constant cathodic potential of −400 mV to obtain sufficiently high current signals. One example of the current responses is shown in Fig. 6. From this the linear NO characteristic (Fig. 7a) and the linear O$_2$ characteristic (Fig. 7b) are simultaneously obtained for the experimental concentration ranges, yielding the NO sensitivity about 14 nA/ppm and O$_2$ sensitivity of 0.02 nA/ppm according to the definitions

$$S_{NO} = \left[ \frac{\partial |I_{NO}|}{\partial \phi(NO)} \right]_{\phi(O_2)} = \left[ \frac{\partial |I_{NO,O_2} - I_{O_2}|}{\partial \phi(NO)} \right]_{\phi(O_2)} \quad (3)$$

$$S_{O_2} = \left[ \frac{\partial |\bar{I}_{O_2}|}{\partial \phi(O_2)} \right]_{\phi(NO)} \quad (4)$$

Here $S_{NO}$, $S_{O_2}$ define the NO sensitivity and the O$_2$ sensitivity of the sensor, respectively, $\bar{I}_{O_2}$ the time average value of the current for each O$_2$ concentration, because it changes with time (Figs. 6 and 8). The definitions of $I_{NO,O_2}$, $I_{O_2}$, $I_{NO}$, $\varphi(NO)$, $\varphi(O_2)$ are illustrated in Fig. 6. Obviously the NO sensor has a high NO sensitivity and very low O$_2$ sensitivity ($S_{NO} \gg S_{O_2}$). This NO sensitivity is much higher than that of the diffusion limiting amperometric NO sensors with two working electrodes, which are reported in the literature [8].

The sensor response to NO, O$_2$, N$_2$ gas mixtures is given by the total current

$$I_{NO,O_2} = S_{NO}[\varphi(NO) + (S_{O_2}/S_{NO})\varphi(O_2)] + I_0 \quad (5)$$

and depends on the ratio $S_{O_2}/S_{NO}$ of the O$_2$ sensitivity and the NO sensitivity, respectively, as defined above (Eqs. (3) and (4)). The offset current (i.e. there is no NO and O$_2$ in the gas mixture) is denoted by $I_0$.
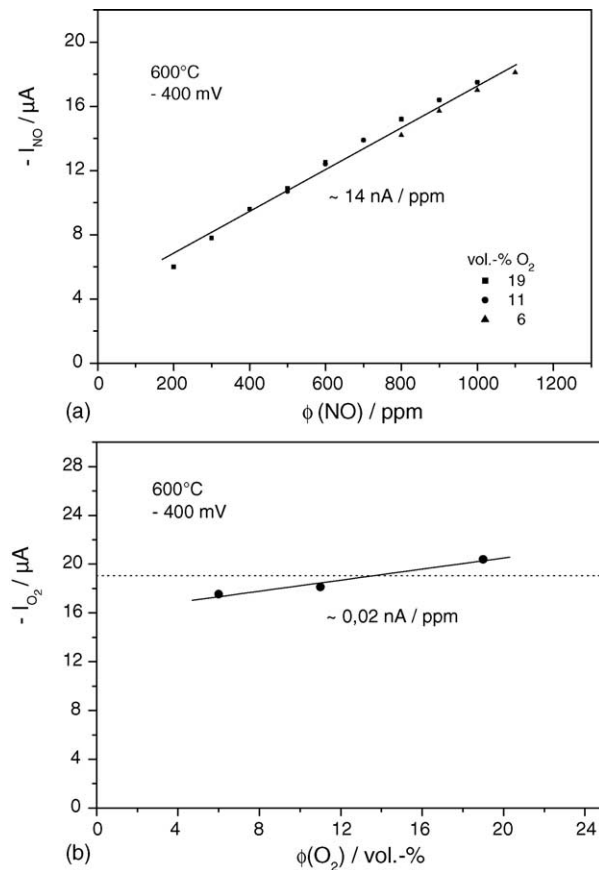


Fig. 7. Simultaneous NO characteristic (a) and O$_2$ characteristic (b) of the amperometric NO gas sensor exposed to various NO, O$_2$, N$_2$ gas mixtures (data taken from Fig. 6. The dashed line in (b) shows the average current response to the O$_2$ concentration.
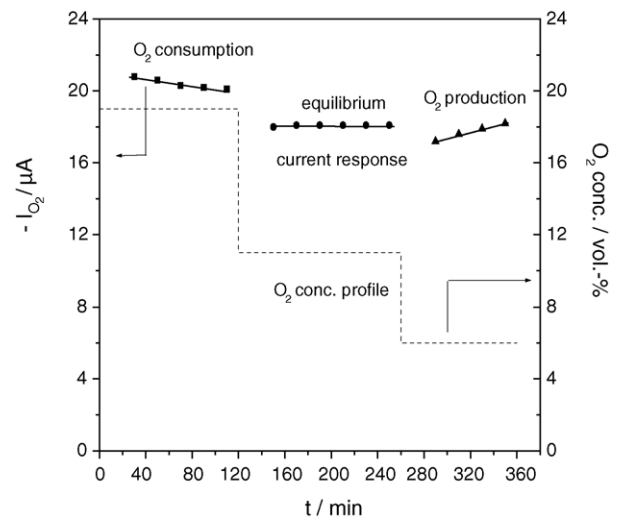


Fig. 8. In-stationary O$_2$ reduction current response $I_{O_2}(t)$ of the amperometric NO gas sensor (solid lines) to the stationary O$_2$ concentration profile (dotted line), corresponding to Fig. 6.

If the sensitivity $S_{O_2}$ of the electrode material is much smaller than the sensitivity $S_{NO}$, as is the case here ($S_{NO}/S_{O_2} \sim 14\,\text{nA ppm}^{-1}/0.02\,\text{nA ppm}^{-1} = 700$), the current response of the sensor to NO, $O_2$, $N_2$ gas mixtures is nearly independent on the $O_2$ concentration:

$$I_{NO,O_2} \approx S_{NO}\varphi(NO) + I_0 \tag{6}$$

as shown in Fig. 7a. Assuming the sensitivity $S$ to depend essentially on the reaction rate $k$, the very low ratio $S_{O_2}/S_{NO}$ means that the NO reaction at the electrode runs faster than the one of $O_2$. Especially the NO dissociation as catalysed by the Rh additive is believed to run faster than the $O_2$ dissociation, which is inhibited by the Au component of the electrode.

The sensor should also respond to $NO_2$, because it is electrochemical reduced to NO and $O^{2-}$ at the cathode. But this has not been tested so far.

The total current $I_{NO,O_2}$ also reflects the dependence of the $O_2$ reduction current on $O_2$ concentration and time (Fig. 6). At 19 vol.% $O_2$ the total current $I_{NO,O_2}$ drops with time for each NO concentration, at 11 vol.% $O_2$ the total sensor current $I_{NO,O_2}$ is stationary for each NO concentration and it raises with time for each NO concentration at 6 vol.% $O_2$. The different time dependencies of the total current correlate with the tendencies of that of the $O_2$ reduction current $I_{O_2}$ (Fig. 8) where $I_{O_2}$ at first decreases for 19 vol.% $O_2$, then remains constant for 11 vol.% $O_2$ and finally rises with time for 6 vol.% $O_2$. However, ideally the sensor should respond to stationary oxygen concentration values (indicated in Fig. 8 by the dashed line) with a constant stationary current (as implied in Fig. 7b by the dashed line) as is the case when Pt/YSZ or Au/YSZ electrodes are used. The observed time behaviour could be caused by a chemical reaction of the electrode surface $S_{RhPtAu}$ with $O_2$ symbolically described by

$$S_{RhPtAu} + \tfrac{1}{2}O_2 \leftrightarrow S_{RhPtAu}\!-\!O \tag{7}$$
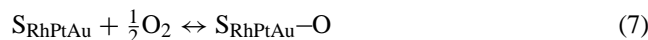
forming some kind of surface oxide. This surface reaction (chemisorption or redox reaction) is reversible depending on the $O_2$ concentration. At high $O_2$ concentration (19 vol.%) the surface oxidation/reduction equilibrium is shifted to the right direction building up $S_{RhPtAu}\!-\!O$ and by $O_2$ consumption leading to a decrease of the $O_2$ reduction current $I_{O_2}$.

During the $O_2$ concentration drop from 19 to 11 vol.% the reaction reverses partially to the left direction resulting in the release of $O_2$. Then, consumption and production of $O_2$ are in equilibrium and $I_{O_2}$ does not depend on time. However, $I_{O_2}$ rises at low $O_2$ concentration (6 vol.%), because the decomposition of the surface oxide $S_{RhPtAu}\!-\!O$ is more convenient.

The NO reduction is slightly influenced by the chemical surface reaction (Eq. (7)), showing a small current decrease with time (Table 1).

## 4. Conclusions

The EIS and LSV studies on the three types of electrodes allow to draw the following conclusions: (1) in comparison with the Pt/YSZ electrode the multi-metallic electrodes PtAu/YSZ and RhPtAu/YSZ have an inhibitor effect on the cathodic $O_2$ reduction according to $R_{ct}(Pt) < R_{ct}(PtAu) < R_{ct}(RhPtAu)$. (2) The RhPtAu/YSZ electrode shows the strongest catalytic effect on the cathodic NO reduction and is therefore a suitable working electrode for NO sensors. The amperometric NO gas sensor RhPtAu/YSZ/RhPtAu shows a high NO sensitivity of about 14 nA/ppm and a low $O_2$ sensitivity of 0.02 nA/ppm. The availability of electrode materials with that behaviour opens up possibilities for the development of highly sensitive amperometric NO gas sensors with single working electrode, i.e. the NO concentration in $O_2$ and NO containing gas mixtures can be directly measured without oxygen pumping from the sensor.

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Table 1
NO reduction current for different $O_2$ concentrations and times

| $\phi(NO)$ (ppm) | $-I_{NO}$ (μA) at 19 vol.% $O_2$, $t = 0$–120 min | $-I_{NO}$ (μA) at 11 vol.% $O_2$, $t = 120$–240 min | $-I_{NO}$ (μA) at 6 vol.% $O_2$, $t = 240$–360 min |
|---|---|---|---|
| 200 | 6.0 | – | – |
| 300 | 7.8 | – | – |
| 400 | 9.6 | – | – |
| 500 | 10.9 | 10.7 | – |
| 600 | 12.5 | 12.4 | – |
| 700 | – | 13.9 | – |
| 800 | – | 15.2 | 14.4 |
| 900 | – | 16.4 | 16.0 |
| 1000 | – | 17.5 | 17.3 |
| 1100 | – | – | 18.4 |

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## Biographies

**P. Schmidt-Zhang** studied physics and received his diploma from the Free University Berlin. He worked in the fields of spectroelectrochemistry, photovoltaic, high temperature electrochemistry, solid state electrochemistry, physical and chemical sensorics. His actual research interests are devoted to the development of electrochemical gas sensors for detection of $NO_x$ and combustibles.

**W. Zhang** received her MS in chemistry from the Beijing University, China and her PhD from the Free University Berlin, Germany. Her research interests are devoted to corrosion, electrically conducting polymer films and electrochemical sensors.

**F. Gerlach** received his diploma in electrical engineering from the Technical University Chemnitz. He designs electronic circuits for special sensors and develops electrochemical sensors for environmental analysis. He is responsible for coating and preparation technologies (evaporation, plasma etching, screen printing) at the institute and he investigates surfaces of new materials by scanning tunnel microscopy (STM).

**K. Ahlborn** received her diploma in chemistry from the Miner Academy Freiberg. She is involved in the development and testing of electrochemical sensors especially for operation under harsh conditions and in the characterisation of new materials using electrochemical methods.

**U. Guth** received his PhD in chemistry from the University of Greifswald in 1975. Since 1993 he worked there as a professor in the fields of solid state electrochemistry and chemical sensorics. In 1999 he got a professorship for physical chemistry at the Technical University of Dresden and became the head of the Kurt Schwabe Institute. His main research interests are dedicated to properties of new materials for high temperature gas sensors and for solid oxide fuel cells.