Effect of the Heterogeneous Catalytic Activity of Electrodes for Mixed Potential Sensors

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The concept of mixed potential sensors bases on the principle that competing reactions form a mixed electrode potential. The exchange of charge carriers takes place at the TPB. However, it is also assumed that heterogeneously catalyzed gas phase reactions reduce the analyte concentration locally. Since this already occurs before the analyte reaches the TPB, the actually detected concentration is not equal to the dosed concentration. This mechanism is investigated in this work using different electrode configurations. Platinum electrodes designed as full-circles are compared with mesh electrodes. The full-circle electrode shows reduced sensitivity, since the high precious metal content probably catalyzes the gas phase reaction more strongly. This was also confirmed by an electrochemical characterization using polarization curves. The sensitivity of the electrode also increases due to higher sintering temperatures and thus reduced porosity, which influences the area available for heterogeneous catalysis. When gold is used as electrode, this mechanism can hardly be observed, since Au shows low catalytic activity towards the oxidation of the used propene. It is shown how heterogeneous catalytic activity of electrodes affects the sensor signal and to what extent a deviation from the conventionally used mixed potential theory is expected at low analyte concentrations.

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Determining the concentration of certain gas components (often denoted as analyte) in a gas mixture is the task of many research activities. Especially in the exhaust gas of automotive applications, this is a challenge due to the harsh conditions. To ensure sufficient chemical and thermal stability, gas sensors based on solid electrolytes are therefore often investigated, with yttrium-stabilized zirconia (YSZ) being used in most cases. Besides methods based on dynamic,2,3 thermoelastic,4,5 and amperometric6,7 measuring principles, especially the field of gas sensors on a mixed potential basis is investigated, as they are characterized by high sensitivity and selectivity.8 This is evident from the immense amount of work published since the first description of non-equilibrium behavior.9 Finally, various electrode materials and sensor assemblies were investigated with regard to the most sensitive and selective detection of ammonia (NH₃),10–13 hydrogen (H₂),14–16 carbon monoxide (CO),17–20 hydrocarbons (HC),21–24 and nitrogen oxides (NOₓ),25–28 as well as components containing sulfur29,30 or mixtures of them.31,32

In principle, the sensor signal of mixed potential sensors is determined on the basis of the different reactions at two electrodes of different materials, see for example Ref. 33 and 34. Another method is to distinguish the reaction in different gas mixtures so that one of the electrodes faces a reference gas atmosphere as described in Ref. 35 or 36. If the electrodes of this method are of equal composition, an electrochemical comparison of two gas atmospheres can be made. We used this method to determine the conversion of automotive aftertreatment systems by comparing the gas mixtures upstream and downstream of a catalytic converter.37,38 According to the theory, the sensor signal then only depends on the ratio of the analyte concentrations at the two electrodes, which could be proven by measurements.39 However, it also became clear that the behavior of the used platinum (Pt) electrodes might deviate from the theory under certain conditions, since the Pt electrodes may cause a gas phase reaction due to their heterogeneous catalytic activity that passively influences the signal formation, as it is described for example by Miura et al.40 Therefore, this paper examines to what extent the configuration of the platinum electrode affects the mixed potential formation and how finally the sensitivity to the electrochemical comparison of two gas atmospheres can be increased. In addition, some theoretical aspects of mixed potential formation are to be considered in more detail.

Mixed Potential Theory for the Electrochemical Comparison of Two Gas Atmospheres

Two propene containing gas mixtures were first compared with Pt electrodes. A mixture of oxygen and nitrogen was used as the base gas. At the three-phase boundaries (TPB), oxygen is then converted into an oxide ion according to Eq. 1, consuming doubly ionized oxygen vacancies V̂O from the YSZ lattice and electrons, \( e^- \). Propene is oxidized to water and carbon dioxide by means of the oxide ions built into the electrolyte as shown in Eq. 2. This again creates oxygen vacancies and electrons.36

\[
\text{O}_2 + 2\text{V}̂O^- + 4e^- \rightarrow 2\text{O}_2^\text{O}^+
\]

\[
\text{C}_3\text{H}_6 + 9\text{O}_2^\text{O}^- \rightarrow 3\text{CO}_2 + 3\text{H}_2\text{O} + 9\text{V}̂O^- + 18e^-\n\]

As a result, a local current flows from the two reactions, which can be described by the Butler-Volmer equation:

\[
j_{\text{O}_2} = j_{0,\text{O}_2} \cdot \left[ \exp \left( n_{\text{O}_2} \cdot \left( 1 - \alpha_{\text{O}_2} \right) \cdot F \cdot \left( \frac{E - E_{0,\text{O}_2}}{R \cdot T} \right) \right) - \exp \left( -n_{\text{O}_2} \cdot \alpha_{\text{O}_2} \cdot F \cdot \left( \frac{E - E_{0,\text{O}_2}}{R \cdot T} \right) \right) \right] \]

\[
j_{\text{C}_3\text{H}_6} = j_{0,\text{C}_3\text{H}_6} \cdot \left[ \exp \left( n_{\text{C}_3\text{H}_6} \cdot \alpha_{\text{C}_3\text{H}_6} \cdot F \cdot \left( \frac{E - E_{0,\text{C}_3\text{H}_6}}{R \cdot T} \right) \right) - \exp \left( -n_{\text{C}_3\text{H}_6} \cdot (1 - \alpha_{\text{C}_3\text{H}_6}) \cdot F \cdot \left( \frac{E - E_{0,\text{C}_3\text{H}_6}}{R \cdot T} \right) \right) \right] \]

In Eqs. 3 and 4, the current density \( j_i \) of the respective reaction \( i \) is calculated from the electrode potential \( E \), the equilibrium potential \( E_{0,i} \), the temperature \( T \), the universal gas constant \( R \), the Faraday constant \( F \), the charge transfer coefficient \( \alpha_i \), the number of transferred charge carriers \( n_i \), the reaction order \( Z_i \), the concentration \( c_i \) and a pre-factor \( A_i \), which contains a temperature dependence according to Arrhenius. Assuming that in the present case oxygen is mostly only reduced and propene is only oxidized, the Butler-Volmer equation can be simplified for the oxygen reaction to the cathodic fraction and the propene reaction to the anodic fraction, as shown in Eqs. 5 and 6.

In this often-used approach to describe the processes, the exchange current density \( j_{0,i} \) is simplified and given as the product of a constant

\[
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\]
with the respective concentration of the gas components:\(^8\)

\[ j_{02,e} = -A_{O_2} \cdot c_{O_2}^{Z_{O_2}} \cdot \exp\left(\frac{-n_{O_2} \cdot \alpha_{O_2} \cdot F \cdot (E - E_{O_2,0})}{R \cdot T}\right) \]  

[5]  

\[ j_{C3H6,a} = A_{C3H6} \cdot c_{C3H6}^{Z_{C3H6}} \cdot \exp\left(\frac{n_{C3H6} \cdot \alpha_{C3H6} \cdot F \cdot (E - E_{C3H6,0})}{R \cdot T}\right) \]  

[6]  

In equilibrium, the net current becomes zero, so the following relationship applies:

\[ j_{O_2,e} + j_{C3H6,a} = 0 \]  

[7]  

If Eqs. 5 and 6 are resolved according to Eq. 7 by the electrode potential, an expression is obtained for the formed mixed potential \( E_{mix} \):

\[ E_{mix} = E_0 + B^* \cdot (Z_{C3H6} \cdot \ln c_{C3H6} - Z_{O_2} \cdot \ln c_{O_2}) \]  

[8]  

The following relationship applies to the two constants \( E_0 \) and \( B^* \) depending on the selected electrode material and the temperature:

\[ E_0 = B^* \cdot \ln\left(\frac{A_{O_2}}{A_{C3H6}}\right) + \frac{n_{O_2} \cdot \alpha_{O_2} \cdot E_{O_2,0} + n_{C3H6} \cdot \alpha_{C3H6} \cdot E_{C3H6,0}}{n_{O_2} \cdot \alpha_{O_2} + n_{C3H6} \cdot \alpha_{C3H6}} \]  

[9]  

\[ B^* = \frac{R \cdot T}{F \cdot (n_{O_2} \cdot \alpha_{O_2} + n_{C3H6} \cdot \alpha_{C3H6})} \]  

[10]  

The measured sensor signal \( U_S \) finally results from the mixed potential difference at the working electrode \( E_{mix,WE} \) and the reference electrode \( E_{mix,RE} \):

\[ U_S = E_{mix,WE} - E_{mix,RE} \]  

[11]  

Assuming that the two electrodes are of the same composition and that the oxygen content for both electrodes is the same and that only the propene concentration at the two electrodes differs, the sensor signal can be calculated as shown in the following equation. For the purpose of clarity, the constant \( B^* \) is also multiplied by the reaction order for \( B \):

\[ U_S = B \cdot \ln\left(\frac{c_{C3H6,WE}}{c_{C3H6,RE}}\right) \]  

[12]  

As will be seen later in the measurements, however, it must be noted that due to various factors, it is not possible to manufacture the electrodes 100% exactly identically. Their morphology may vary slightly due to varying layer thickness, sintering position or other factors. The reaction locations for Eqs. 1 and 2 are therefore not identical, which mainly influences the pre-factors \( A_{C3H6} \) and \( A_{O_2} \). Finally, according to Eq. 9, the constants \( E_0 \) for the two electrodes will also differ and generate an offset voltage \( U_{off} \):

\[ U_{off} = E_{0,WE} - E_{0,RE} \]  

[13]  

Therefore, Eq. 12 can be corrected by the offset voltage:

\[ U_S = B \cdot \ln\left(\frac{c_{C3H6,WE}}{c_{C3H6,RE}}\right) + U_{off} \]  

[14]  

For the case of a very low propene concentration at the working electrode, the sensor signal would, according to this simplification, reach a very high value. However, the assumption that only the cathodic part can be used to calculate the current density of the oxygen reaction no longer applies here. In fact, the anodic content must also be taken into account as well. Furthermore, for a very small propene concentration at the working electrode, the current density of the propene reaction becomes negligibly small, whereby Eq. 7 states that the current density of the oxygen reaction must be small as well. This condition is reached when the electrode potential corresponds to the equilibrium potential. In this case, the mixed potential at the working electrode becomes:

\[ c_{C3H6,WE} \approx 0 \Rightarrow U_{S,max} = E_{0,WE} - E_{0,RE} - B^* \cdot \ln\left(\frac{c_{C3H6,RE}}{c_{O_2,RE}}\right) \]  

[15]  

Finally, the sensor signal depends no longer only on the ratio of the working and reference electrode concentrations, as described in Eq. 14, but also on the analyte concentration and oxygen concentration at the reference electrode:

\[ c_{C3H6,WE} \approx 0 \Rightarrow U_{S,max} = E_{0,WE} - E_{0,RE} - B^* \cdot \ln\left(\frac{c_{C3H6,RE}}{c_{O_2,RE}}\right) \]  

[16]  

In order to calculate the range near the limiting case, the mixed potentials would have to be determined with the current densities for anodic and cathodic components, as shown in Eqs. 3 and 4. In this transition area, a different sensitivity of the electrode will finally also occur, as shown in the diagram in Fig. 1 and seen many times in literature.\(^40\)

For small analyte concentrations, the induced current density is so small that no potential change compared to the equilibrium potential of the oxygen reaction according to Eq. 1 can be measured. The sensitivity is zero in this case (see concentration range (A) in Fig. 1). If the analyte concentration is high enough to determine a measurable potential change, the mixed potential is formed from the competing reactions according to Eqs. 1 and 2. However, since the induced current due to oxidation of the analyte Eq. 2 is still low, the overvoltage is also comparatively low. Therefore, the correct calculation of the mixed potential is given by the current densities of Eqs. 3 and 4. They must cancel out each other. The simplification from Eq. 7 is often used in literature but it does not take into account the anodic part of the oxygen reaction or the cathodic part of the analyte reaction. The sensitivity is therefore lower than it is for the case of comparatively high concentrations, where the simplification that only the anodic part of the analyte oxidation or cathodic part of the oxygen reduction is valid.
Setup to Compare Electrochemically Two Gas Mixtures

The development of a sensor that is excellently suited for the electrochemical comparison of two gas atmospheres was described in detail in Ref. 38. Such a sensor device is shown in Fig. 2. The basic design consists of a YSZ disc with a diameter of 42 mm and a thickness of 1 mm. An integrated heater is provided as described in Ref. 38. The heater allows sufficiently high temperatures in the center of the disc for ionic conductivity and electrode activity. It is embedded centrally in the YSZ ceramic and is electrically insulated to heat both surfaces of the disc equally and to avoid electrochemical blackening. The electrodes are located in the center of each disc, with insulated leads leading to the rim of the ceramic where the contact wires are bonded. In the complete measurement setup, only the electrodes are in contact with the gas atmosphere. The heater is therefore designed in a way that the rim of the disc is cold enough to apply a low-temperature sealing in front of the contacting and finally to ensure uncomplicated hermetic sealing and separation of the two gas mixtures. This is possible because of the low thermal conductivity of YSZ. The electrodes, like heater and insulation, are deposited by screen-printing. The RE and WE should therefore hardly differ in morphology and material. Nevertheless, the electrodes can never be equal.

As shown in the scheme in Fig. 3, the measurement setup is realized with two housings made of polyether ether ketone (PEEK). The sensor is pressed between the housings by means of a screwable clamp, whereby two conventionally used O-ring sealings between the PEEK housings and the sensor disc allow the hermetic sealing of the gas compartments. Finally, two half-cells are formed, hereinafter referred to as half-cell 1, which contains the reference electrode (RE), and half-cell 2, in which the working electrode (WE) is located. The construction is characterized by a low dead volume, chemical and thermal stability, simple device replacement and the fact that the wires for contacting the heater or electrodes are not exposed to the gas. For more details regarding the measurement setup, the reader is referred to Ref. 39, where this setup has already been described in detail.

The two gas mixtures were dosed with mass flow controllers (MFC). The base gas consisted of a mixture of 15% O2 in N2, to which the analyte was added. The diagram in Fig. 4 shows a usually used profile of the two analyte concentrations. The reference atmosphere in half-cell 1 was dosed constantly over one profile, while the gas concentration in half-cell 2 was varied in steps. A mixture containing propene was chosen as reference (not only, e.g., air) to prove by measurements the relationship in Eq. 14. The sensor signal is thus only dependent on the ratio of the two analyte concentrations. Therefore, different reference concentrations are also investigated. The scheme in Fig. 1 shows that a signal deviation from the conventional theory can be expected at low concentrations. The reference is therefore realized with several hundred ppm so that the expected mechanism of lower sensitivity is not superimposed for WE and RE. Thus, it should be possible to characterize unambiguously the effect of heterogeneous catalysis, especially at low analyte concentrations.

Sensor Behavior with Pt Full-Circle Electrodes

The sensor signal is measured using a concentration profile as shown in Fig. 4. To vary the ratio of the analyte concentrations, this
Figure 5. Sensor signal over the propene concentration ratio for different reference concentrations $c_{C_3H_6,RE}$. Symbols represent values derived from measurements, while the line is an approximation according to Eq. 14, with parameters as indicated.

profile was run through with several reference concentrations $c_{C_3H_6,RE}$. For evaluation, the sensor signal was averaged for each step. A detailed look at typical raw measurement data is given in the appendix. Independently of the applied reference concentration, the sensor signal should be the same if the ratio $c_{C_3H_6,WE} / c_{C_3H_6,RE}$ is the same, as described by Eq. 14. This becomes clear from Fig. 5. In the diagram, the averaged sensor signal for each step is plotted over the propene concentration ratio, with the various symbols representing different reference concentrations $c_{C_3H_6,RE}$ in half-cell 1. By means of the drawn line, which was calculated using Eq. 14, it becomes clear that the above-explained theory corresponds as far as possible with the measured data. The sensor signal therefore depends only on the ratio of the concentrations in the two gas atmospheres and not directly on the reference atmosphere.

If the measured sensor signal is plotted over the logarithm of the propene concentration ratio, the voltage signal vs propene concentration ratio becomes a straight line with a slope $B$ between $-12 \text{ mV/decade}$ and $-18 \text{ mV/decade}$ and an offset voltage $U_{\text{off}}$ between $-1 \text{ mV}$ to $-8 \text{ mV}$. If the ratio of $c_{C_3H_6,WE} / c_{C_3H_6,RE}$ becomes less than 0.02, however, the approximation curve becomes a horizontal line. This behavior is even more pronounced the higher the sensor temperature is, which is especially clear from the upper diagram in Fig. 6 (500$^\circ$C). Furthermore, it can be seen that the slope and offset of the calculated curve decreases with increased temperature. In addition, the measurement deviates from the calculated curve at a higher ratio $c_{C_3H_6,WE} / c_{C_3H_6,RE}$. While the first deviations can be seen at about 0.04 at 450$^\circ$C, the measured values at 500$^\circ$C no longer follow the model presented even at 0.1.

The measured values that are no longer located on the model curve calculated according to Eq. 14, have not experienced a significant signal increase even though the ratio of the concentrations was reduced. Therefore, the sensor voltage depends only on the reference atmosphere, while the potential of the working electrode follows the thermodynamic equilibrium of the oxygen reaction according to Eq. 1. The propene concentration $c_{C_3H_6,WE}$ is therefore negligible here (see (A) in Fig. 1). The potential for these cases can only be described by the theory according to Eq. 16. For this purpose, the maximum sensor voltage, which can be achieved, was calculated with Eq. 16.

Figure 6. Sensor signal using a Pt full-circle electrode (sintered at 975$^\circ$C) vs. the logarithmic ratio of propene concentrations for different reference concentrations $c_{C_3H_6,RE}$ and different sensor temperatures. Symbols represent values derived from measurements, while the solid line is an approximation according to Eq. 14, with each parameter being given in the equation. The dashed lines indicate possible maximum sensor voltages, for example at $c_{C_3H_6,RE}$ of 250 ppm and 750 ppm, calculated according to Eq. 16.
Fig. 6, the maximum sensor voltage was determined using the reference concentrations of 250 ppm and 750 ppm as an example. For the parameter $P'$ in Eq. 16, $-12$ mV/decade was chosen for the measurement at 500°C, since this value was also used for the corresponding model curve according to Eq. 14. It can be seen that the calculated maximum sensor voltages for reference concentrations of 250 ppm and 750 ppm fit with the measured values. Especially the difference of the maximum sensor voltage at reference concentration of 250 ppm and 750 ppm is approximated with $-12$ mV/decade, which means that the RE has the same sensitivity compared to the WE.

Since the measurements with the three different sensor temperatures from Fig. 6 were conducted with the same concentration profile, the question arises why the slope of the model curves calculated with Eq. 14 decreases with increasing temperature. According to Eq. 10, the slope should rather increase, while the deviation of measured values from the calculated curve already occurs at supposedly higher $c_{C3H6,RE}$.

The fact that the measured values do not follow the calculated curves according to Eq. 14 but are horizontal suggests that there is a kind of transport limitation. This means that the propene concentration dosed in half-cell 2 does not reach the TPB at all and thus the propene cannot be converted to carbon dioxide and water:

$$C_3H_6 + 4.5O_2 \rightarrow 3CO_2 + 3H_2O$$

[17]

No charge carriers are exchanged and finally this reaction has no direct impact on the signal formation. A scheme of possible processes at the electrode and the TPB is shown in Fig. 7. This has already been presented in a similar form in the literature.3 Propene and oxygen diffuse into the porous platinum electrode from the right, whereby the concentration $c_{C3H6,S}$ almost equals the dosed amount. Along the electrode, i.e. between TPB and free gas phase, it is possible that Pt catalyzes the gas phase reaction according to Eq. 17. As a result, the concentration of the analyte is reduced locally, as shown in the diagram in Fig. 7. Furthermore, oxygen can adsorb at the electrode and can be incorporated into the electrolyte as an ion, as already shown in Eq. 1. At the three-phase boundary itself, propene can now be converted with the oxygen ions according to Eq. 2, whereby charge carriers are exchanged and actively influence the electrical potential of the electrode. The said gas phase reaction also passively influences the potential, since it changes the propene concentration $c_{C3H6,S}$ at the surface. This eventually leads to the signal formation at the TPB.

These processes would also explain the temperature-dependent characteristics of the measurement shown in Fig. 6. The kinetics of the gas phase reaction increases exponentially with temperature. Therefore, this effect is less distinct at a sensor temperature of 400°C compared to 500°C. The potential formation is determined on the one hand by the resulting mixed potential, where Eq. 14 applies. On the other hand, if the catalytic effect of the electrode is too high and the analyte concentration is therefore greatly reduced, the potential is determined only by the thermodynamic equilibrium of the oxygen reaction, Eq. 16 applies to this. In between, there is a crossover region characterized by a sensitivity that decreases with decreasing analyte concentration (see (B) in Fig. 1). This phenomenon is also observed in the literature, e.g. two different sensitivities are mentioned, where those for low concentrations are also lower.41,42 Therefore, the slope of the model curve with increased sensor temperature probably decreases as well, since the crossover region (cf. (B) in Fig. 1) is already reached at higher analyte concentration, while at low temperature the mixed potential formation (cf. (C) in Fig. 1) over the entire measured concentration range is still mainly dominant. Furthermore, it should be taken into account that the catalytic activity also depends on the concentration of the gas component and is therefore not the same over the entire measuring range. The propene concentration is then reduced by a different factor at low concentrations than it is the case for high concentrations.

**Reduction of the Catalytic Activity of the Platinum Electrodes**

In order to support the just presented theory, an experimental attempt was first made to reduce the catalytic activity of the electrode. For this purpose, the electrodes were geometrically modified. They can, for example, be designed as a circular mesh (see image in Fig. 8). Furthermore, the mesh was manufactured with a smaller layer thickness. The latter can be achieved comparatively easily through the screen-printing process. The diameter of the mesh is the same as that of the full-circle electrode shown above. However, the amount of platinum should be significantly reduced, while the open structure may even improve diffusion to three-phase boundaries. The edges of each knot of the mesh should therefore only consist of three-phase boundaries. Only the lines of the lattice can lead to a gas phase reaction through catalytically active platinum, whereby a diffusion through to the TPB is also possible here.

The measurements on the Pt mesh electrodes with different sensor temperatures and varying reference concentrations conducted analogously to the investigations on the full-circle electrode (see Fig. 6) are shown in Fig. 8. It can be clearly seen that, independently of the sensor temperatures used here, the respective measuring values can be approximated with the presented theory of Eq. 14. Therefore, even for small concentrations in half-cell 2, the sensor signal depends only on the ratio of the concentrations in the two half-cells and not only on the reference atmosphere. Obviously, with the modified geometry it is possible to keep the gas phase reaction according to Eq. 17, whereby compared to the full-circle electrode more analyte reaches the TPB. Finally, even at 500°C sensor temperature, an increase of the signal up to the ratio $c_{C3H6,WE}$/$c_{C3H6,RE}$ of 0.005 can be detected. With regard to the presented possibilities for calculating the mixed potential, the assumption in region (C) of the diagram shown in Fig. 1 applies here over the entire measured concentration range.

In Fig. 6 and Fig. 8, also the offset voltage $U_{AE}$ is of interest. Interestingly, it is the highest for the lowest temperature of 400°C, which comes along with the highest slope with respect to the model curve. Measurements at 500°C, on the other hand, show the smallest offset voltages and the smallest slope of the model curves was found.
Figure 8. Sensor signal using a Pt mesh electrode (sintered at 975°C) vs. the logarithmic ratio of concentrations for different reference concentrations \(c_{\text{C}_3\text{H}_6, \text{RE}}\) and different sensor temperatures.

here. This is shown in Fig. 9, where the absolute value of the offset voltage is plotted over the absolute value of the slope of the respective model curve at the three sensor temperatures. The trend shows an increased offset voltage with increasing sensitivity. In relation to Eqs. 9 and 13, however, this relationship applies also to the theory presented. If the value of \(B^*\) increases, at a constantly deviating kinetics of the pre-factors \(A_{\text{C}_3\text{H}_6}\) und \(A_{\text{O}_2}\) at the two electrodes, the offset voltage increases directly proportional. This also explains the increasing offset at a lower sensor temperature that is related to an increased slope of the model curve.

Comparison of Full-Circle and Mesh Electrode on Polarization

The effect of the heterogeneous catalyzed gas phase reaction that locally reduces the analyte concentration can be quantified by electrochemically characterizing the system. For this purpose, polarization curves were obtained at the two presented systems of the full circle and the mesh electrode. The recorded values are shown in Fig. 10. The currents resulting from the oxygen reaction according to Eq. 1 are mostly the same for the two electrode configurations. This is an indication that using the mesh electrode, the total resistance of the system hardly changes. The values shown for the propene reaction according to Eq. 2 were determined by measuring the currents in the mixture with oxygen. To isolate the current values for the propene reaction, the measured values in the mixture were reduced by the corresponding measured value in the base gas measurement. The level of the propene-induced current is significantly higher with the mesh electrode than is the case with the full-circle electrode. The exchange current density \(j_{0, \text{C}_3\text{H}_6}\) for the mesh electrode can be estimated at about 0.0335 A/m², while for the full circle it is only 0.0137 A/m². These values do not initially meet the expectations, since one could assume that a lower electrode resistance is achieved by the full-circle electrode, since more area is available for reaction sites. However, one could assume that the kinetics \(A_{\text{C}_3\text{H}_6}\) of the propene reaction according to Eq. 2 is basically the same for the two electrode configurations, while perhaps it is even higher for a larger area like here for the full-circle. This is valid because the platinum electrodes were printed with the same screen printing paste and manufactured and fired under the same conditions. Then, according to the following simplification from Eq. 6 for the exchange current density, only the propene concentration may have been reduced.

\[
 j_{0, \text{C}_3\text{H}_6} = A_{\text{C}_3\text{H}_6} \cdot \frac{Z_{\text{C}_3\text{H}_6}}{c_{\text{C}_3\text{H}_6}} \]  

If kinetics \(A_{\text{C}_3\text{H}_6}\) and exponent \(Z_{\text{C}_3\text{H}_6}\) were identical for full circle and mesh electrode, the concentration at the full circle electrode would have to be reduced by about one third (compared to the mesh electrode) by the heterogeneous catalyzed gas phase reaction according to the determined current values. This could proof the existence of the already postulated heterogeneous catalytic effect of the electrode.8
The activity for the gas-phase reaction for the full-circle electrode must be higher compared to the mesh electrode, as otherwise such a lower current value is not possible. This also explains why the sensor signal hardly increases at small concentrations when using the full circle electrode in Fig. 6. Before the dosed propene reaches the TPB, it is reduced to such an extent by the gas phase reaction that hardly any analyte is involved in the charge carrier exchange to cause a measurable signal change. This is also consistent with the results of Elumalai et al., where an analogous behavior was seen with changes in the thickness of the electrode. The intersection of the current flow induced by propene and oxygen in Fig. 10 shows the theoretically resulting mixed potential. As already shown in the above explanations, the maximum possible mixed potential for the mesh electrode is higher compared to the full circle.

Alternate Ways to Reduce the Catalytic Activity of the Electrodes

Platinum mesh electrodes were fired at a higher temperature of 1200°C as further evidence to validate the presented theory. The upper diagram in Fig. 11 shows the evaluation of a measurement with such electrodes analogous to the measurement conducted above. Again, the measured values can be approximated according to Eq. 14, so that the sensor signal depends only on the ratio of the concentrations in the two half-cells.

The porosity of the platinum layer is expected to be reduced by the higher sintering temperature as compared to a Pt mesh electrode that was fired at a lower temperature as it was illustrated in Fig. 8. From optical investigations, it can be assumed that thereby the porosity was reduced from about 20% to less than 10%. In conclusion, the gas phase reaction according to Eq. 17 should be reduced in accordance with the scheme in Fig. 7. As a result, comparatively more propene reaches the TPB and the charge carrier exchange induced by the Eq. 2 is higher, which also increases the maximum mixed potential that can be achieved. This can be seen from the slope of the calculated curve in Fig. 11, which here with −16 mV/decade is higher for the Pt electrode sintered at 1200°C than for the Pt electrode sintered at 975°C with −8 mV/decade (shown in Fig. 8).

The effect of the reduced gas phase reaction due to a higher sintering temperature and thus due to a reduced porosity and lower surface can be further enhanced by using a catalytically inactive material. Therefore, gold mesh electrodes were considered. Results are shown in the lower diagram in Fig. 11. Its catalytic activity against propene is limited compared to platinum (compared for example according the light-off temperatures for Au and Pt doped catalysts), which means that the gas phase reaction according to Eq. 17 can also be mostly neglected. Therefore, the sensitivity increases significantly in this case, as can be seen from the slope of the calculated curve in the
However, studies on this problem are examined in more detail in a future paper.

Conclusions

This study shows to what extent the heterogeneous catalytic activity of an electrode material has an effect on the signal formation of a mixed potential sensor. For this purpose, platinum full-circle electrodes were initially used for measurements, whereby the deviation from common theories of mixed potential formation was clearly demonstrated. It could be shown to what extent this mechanism affects the signal differently at small and large analyte concentrations and sensing temperatures. If a sensor characteristic was recorded for calibration, deviations at small or large concentrations could be explained. An increase in sensitivity was achieved by reducing the catalytically active platinum quantity with the possibility of better access to the three-phase boundary. Equally successful is the use of a higher sintered platinum electrode, as well as the use of gold as electrode material. In summary, it has been shown to what extent adaptations in morphology, geometry, and material influence the sensitivity of the electrode.

Furthermore, an initial reaction model was presented that could explain the possible processes taking place. Especially with small analyte concentrations, the sensor characteristics usually change, whereby the normally used approach to mixed potential theory is probably not sufficient. While in this case, the oxygen reaction to the cathodic part and the analyte reaction to the anodic part are reduced, for small concentrations both parts have to be considered. For this purpose, a finite element model was created which contains gas reactions, gas diffusion, electrical properties and the necessary electrochemistry. It shows that the here-presented evaluations correspond to the measurement results, so that it is possible to model the mixed potential at the electrodes with the assistance of the theory. Due to the high sensitivity of the sensor material, it has to be described in more detail in a future publication. In addition, the characteristics of gas mixtures and various sensor temperatures, electrode materials, and other possible influences are investigated in more detail.

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Appendix

The plot in Fig. A1 shows the raw data measured over one measurement profile. The upper graph shows the analyte concentrations in both half-cells. They were determined by a FID. The lower diagram shows the measured sensor signal using a mesh Au electrode. The sensor signal immediately follows the stepwise change in the analyte concentration in half-cell 2, while the response time until 90% of the stationary sensor signal is reached is 2 s for the high concentrations at these stepwise changes, while up to 80 s was determined at 3 ppm analyte concentration. The response time with the stepwise change at high concentration is very fast due to the low dead volume of the setup. The sensor setup shows reproducible values when the concentration is increased again, the recovery time until 90% of the stationary sensor signal is reached again can be estimated to about 10 s.

Figure A1. Example for raw data, while a concentration profile is applied as it was described in the text.

shown evaluated data in the lower diagram in Fig. 11 is given by the averaged values of the sensor signal according to each step.

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