# The development of a Nafion based amperometric carbon monoxide sensor for domestic safety

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**A carbon monoxide sensor using Nafion solid polymer electrolyte is described. The proposed manufacturing technology, compatible with hybrid technology, is suitable for cheap mass fabrication.**

Carbon monoxide is a colourless, odourless, toxic gas whose primary source is the incomplete combustion of fossil fuels. Indoors this gas can be a potential problem in any house that uses combustion appliances for heating or cooking or that has an attached garage from which exhaust fumes from an idling car can enter the house.

The acute toxicity of carbon monoxide is well known, but also exposure to low concentrations can cause serious health problems. The toxicity of carbon monoxide is based on its impeding the transport of oxygen by haemoglobin in blood as it has an affinity towards haemoglobin which is approximately 250 times greater than that of oxygen. Long term exposure to even low concentrations of carbon monoxide will therefore lead to an accumulation of the amount bound to haemoglobin. With symptoms like headache, fatigue, nausea, and dizziness that resemble many common illnesses, low-level CO poisoning is easily misdiagnosed and mistreated.

At present carbon monoxide sensing devices are readily available for many industrial applications. The sensors used in these devices include electrochemical sensors, semiconductor sensors, colorimetric detectors and infra red detectors. For domestic safety applications however, only a few systems are available. In addition to good sensor characteristics like a low detection limit, good selectivity, fast response, and good stability, important features are a low power consumption, and a low price. The last two features enable the application of the sensors in affordable battery operated devices. Electrochemical sensors can meet most of these demands, but their high price and need for recalibration seriously hinder their breakthrough in this field.

## Principle of operation

The electrochemical detection of carbon monoxide is based on the reaction of the gas at the sensing electrode. The current that is generated is a measure for the amount of carbon monoxide. The gas has to diffuse from the environment through a diffusion barrier and then reaches the electrode surface. The electrode is a so called gas diffusion electrode. These are gas permeable electrodes made of a catalyst material and a Teflon binder. The carbon monoxide that reaches the electrode surface is oxidized according to:

$$CO + H_2O \rightarrow CO_2 + 2\ H^+ + 2\ e^-$$

To balance this reaction, at the counter electrode, oxygen is reduced:

$$^1/_2\ O_2 + 2\ H^+ + 2e^- \rightarrow H_2O$$

which makes the overall reaction:

$$CO + {}^1/_2\ O_2 \rightarrow CO_2$$

## Classical sensor architecture

The classical amperometric carbon monoxide sensor as is described in [1], is a three electrode version. Because of the electrode reaction, a combined counter and reference electrode does not maintain a constant potential. Therefore a separate reference electrode is necessary. All three electrodes are gas diffusion electrodes, catalysed with platinum black. The electrolyte is sulfuric acid with a concentration of about 5 M. The sensing anode is in contact with air via a gas diffusion barrier. The reference electrode is shielded from carbon monoxide and is kept in a constant environment and therefore maintains a constant potential. For the counter reaction, sufficient supply of oxygen is important. In order to attain the necessary electrode configuration, the sensing electrode is made on a separate sheet of permeable Teflon tape and is facing the sample gas. The counter and reference electrodes are either together on a permeable Teflon sheet at the other side (in contact with the air inside the instrument, see Fig. 1), or inside the sensor cell on separate sheets.

The existing devices function rather well with a detection limit of 1 ppm or less and a response time (90%) of about 30 – 60 s. For non-industrial applications the only compound that has a high cross-sensitivity is alcohol. This cross-sensitivity can be completely suppressed by employment of an




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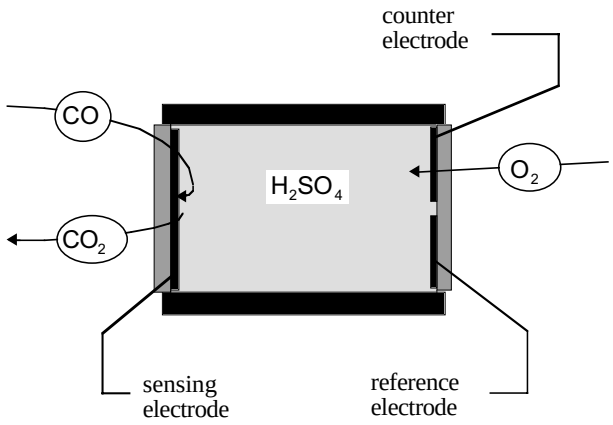


**Figure 1. Schematic representation of classical amperometric carbon monoxide sensor.**

active carbon filter. As during the reaction of carbon monoxide, there is no net change in the sensor itself, the lifetime of the sensor is in theory not limited.

The high cost-price is caused by the complexity of fabrication necessitating the assembly to be done mainly by hand. Further, with sulfuric acid as the electrolyte, special care needs to be taken that the device is properly sealed. The main goal of our work was to investigate the possibility to simplify the fabrication of the sensors giving special attention to mass-production technologies, thus enabling a potential low cost-price.

## Sensor designs using solid polymer electrolyte

After the development of the classical amperometric carbon monoxide sensor, only a few other sensor designs have been described in the literature. Most of these are based on the replacement of the liquid acid electrolyte with a solid state protonic conductor (SSPC) membrane.

Of the SSPC materials known at this moment, the perfluorosulfonate ionomers in our opinion have the best properties in terms of conductivity and chemical resistance. Nafion materials, a trademark of DuPont de Nemours, were developed for fuel cell applications and are produced in sheet form. They are available in different equivalent weights (weight of resin per ion exchange site). The backbone of the polymer is polytetrafluorethylene and has side chains with a sulfonic acid moiety. Despite it being a linear polymer it is not soluble in solvents because of the high crystallinity of the polymer chain. Under special conditions it is possible to dissolve the material [2]. At present, Nafion with an equivalent weight of 1100 is commercially available in solution form. This material is convenient for deposition on electrode surfaces by solvent casting. When the solvent cast material is used however, one should realize that the material properties are different from the original sheet-form [3]. Even after the recommended heat cure at 120 – 130 °C the properties are different.

Usually the sensor construction is the same as the conventional sensor with the electrodes at both sides of the electrolyte, now a polymer sheet. Sensor designs with [4,5] and without [6] a water reservoir have been described. The reason for the application of a water reservoir is the dependency of the sensor sensitivity and noise level on changes in the relative humidity. Changes in the relative humidity affect the proton conductivity and the permeability of the reactant and product gasses in Nafion. In theory it is possible to compensate for the humidity dependency of the sensor response, as it has been found that there is a linear relationship between the two [6,7]. However, changes in noise levels cannot be compensated for, also measurements at extreme low humidities (below 10%) are impossible.

A different sensor design is described in [8]. In this particular case Nafion is solvent cast over a solid state substrate (glass or alumina) with all three electrodes integrated on it. Carbon monoxide now has to diffuse through the thin film of Nafion to reach the sensing electrode. As all three electrodes are exposed to the sample gas now, the reference electrode cannot be made of the same platinum material as the sensing electrode. Gold was found to function satisfactory for this purpose. This simple design has as an advantage that it is easy to make with silicon technology hence ready for cheap mass-production. However, the sensors do not only suffer from problems mentioned above for the dry Nafion sensors, but there is also a slow decay of the sensor signal [9,10]. Even with a laminate structure as was proposed in the literature, a sufficient stability was not observed [11].

## Presentation of present work: Development of a sensor based on a ceramic substrate, gas diffusion electrodes and solvent cast Nafion

The sensor layout is given in figure 2. The three platinum catalyzed gas diffusion electrodes are integrated on an impermeable ceramic substrate with dimensions 22 × 15 mm. Under the sensing and the counter electrode areas several holes (20 respectively 27) with a diameter each of approximately 150 μm were made using a laser. The reference electrode is shielded from the sample gas and its potential remains stable. The Nafion electrolyte is solvent cast over the electrodes and the sensor is completed with a water reservoir with a diameter of 10 and a height of 40 mm, giving a volume of about 3 mL.

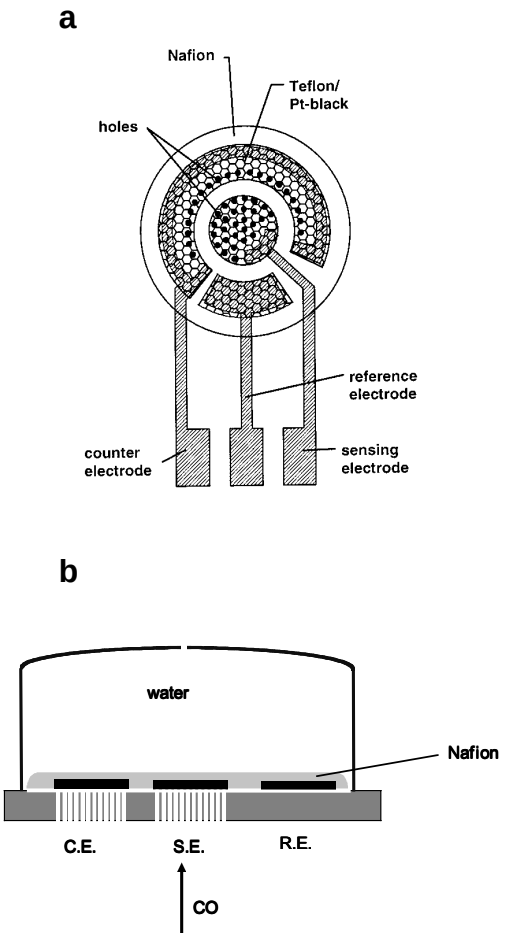


**Figure 2. Layout of the current sensor: (a) top view with the holes, platinum current collectors, Teflon bonded platinum-black electrodes and Nafion, (b) cross section showing the ceramic substrate with the holes, electrodes, Nafion film and the water reservoir.**

### *Sensor fabrication*

The fabrication is a slightly modified version of what was published earlier [11]. A brief description of the materials and fabrication is given below:

The base substrate was standard ceramics (96% alumina, 0.635 mm thick). Wafers of this material were laser scribed and holes were laser drilled. The platinum current collectors were deposited by thick film technology (screen printing and firing). The holes were filled with Teflon particles with an average size of 0.185 – 0.235 μm. This is done by dipping the substrate in a dispersion of the Teflon particles followed by heat-curing. The three gas permeable Teflon bonded platinum black electrodes were painted on the substrates and also heat cured. Over all three electrodes a Nafion membrane was solvent cast using a dispenser. Also the Nafion received a heat treatment. Finally a polymer tube was glued to the substrate and filled with deionised water.

The sensors were operated using a potentiostat with the sensing electrode polarized at 0 V *vs*. the platinum-black reference electrode. When not in use, the three electrodes were short-circuited. The tests were performed in a constant flow of synthetic air, with 0, 100, and 500 ppm CO respectively.

### *Sensor properties*

Sensor sensitivities are typically in the order of 3 – 7 nA/ppm. The detection limit, defined as twice the noise level is in the order of 0.2 – 0.8 ppm CO. Response time $t_{90}$ is between 20 and 90 s, depending on the thickness of the gas diffusion membrane and the Teflon bonded platinum black electrode material. The humidity influence was found to be negligible for relative humidities between 0 and 95%. Small and relatively slow changes in pressure (as variations in the atmospheric pressure) also have a negligible influence on the sensor response. A long term test of one of the sensors is presented in figure 3, the sensitivity given in the figure is calculated per ppm. During the (ongoing) test period of 3 years the sensitivity stayed constant within ± 5%. The water loss because of evaporation was approximately 3 mL per year, necessitating topping up of the reservoir every year. The temperature dependency of the signal is less then 0.2%/ºC.

### *Discussion*

In our approach all three gas diffusion electrodes are integrated on a solid state substrate, with the substrate only gas-permeable under the sensing and counter electrode. In the tested carbon monoxide concentration range (0 – 500 ppm) this yielded a linear signal. Long term exposure (5 hours) did not show any oxygen starvation. Also a version with only holes over the sensing electrode gave similar results. From this it can be concluded that sufficient oxygen can enter via the holes and that carbon monoxide does not reach the reference electrode.

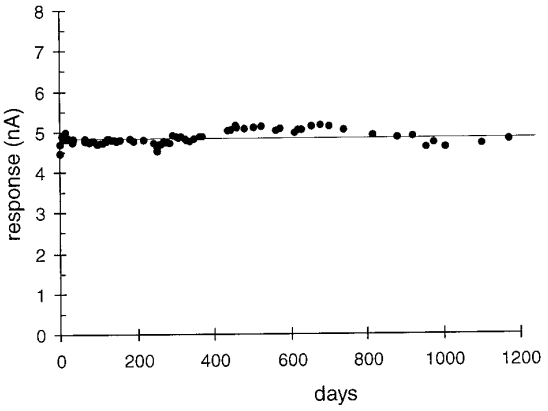


**Figure 3. Long term test of the sensor. Sensitivity is calculated per ppm CO.**

The advantage of this sensor architecture is that all three gas diffusion electrodes can be deposited in one step. Until now the platinum catalysed gas diffusion electrodes are made on permeable Teflon tape by spraying or spreading of the Teflon/platinum-black slurry. By adding thickening agents, we were able to formulate a paintable slurry. Another advantage is that the ceramic base substrate has the current collectors already printed on it. This is much more simple than pressing thin platinum wires in the catalyst material as is normally done. Further, with Nafion/water as the electrolyte the sealing is less demanding than with the corrosive sulfuric acid.

Some unexpected features of the sensor proposed here are the excellent signal stability and the low temperature dependency. This enables the use of such sensors without frequent recalibration and without temperature compensation.

Normally electrochemical carbon monoxide sensors need frequent recalibration, albeit that when sensors are exposed to an aggressive industrial environment this is bound to give more stability problems than in case of installation inside a home. However, also a change in sensitivity in the beginning of the sensors' lifetime, "the burn-in period", as is usually observed for the conventional sensors was not observed here. Further the temperature dependency is rather low compared to values from existing devices. Recently the temperature dependency of electrochemical gas sensors was discussed as part of a study of the mass transport in electrochemical gas sensors [12]. The gas has to diffuse from the air sample via the different diffusion barriers to the electrode surface. It was found that in the conventional sensors about 70% of the transport control is provided by the thin electrolyte film between the pores and the electrode surface. The temperature dependency of the sensors was found to support this assumption. If the gas diffusion barriers control the mass transport this can be according to Fickian or Knudsen diffusion in which case the signal would have a temperature dependency proportional to $T^{0.5}$ or $T^{-0.5}$, respectively [12]. It was found that the temperature dependency of the conventional sensor is proportional to $T^{2.8}$ (also found by us for another commercially available sensor). As is shown in figure 4, the temperature dependency of the Nafion based sensor described here comes close to the values given by Fickian diffusion. Without further study of this effect it is impossible to say anything conclusive, but this is a strong indication that the transport control is now more provided by the gas diffusion barrier instead of the electrolyte film.

### *Limitations and outlook*

The use of Nafion electrolyte in combination with a water reservoir also has its limitations. The device can only be used at temperatures above the freezing point. The addition of a non-alcoholic antifreeze to the water reservoir is at the moment under investigation. Although the sensor is foreseen to be used in a fixed upright position, a wick needs to be implemented in the sensor design, to make sure that the Nafion is always in direct contact with water. Further, because of water evaporation, the lifetime is limited by the volume of the water reservoir. With the choice of materials described here, the loss of water is 3 mL per year. To increase the lifetime possible solutions are: a reduction of the porosity of the ceramic substrate, a larger water reservoir or topping up by the user.

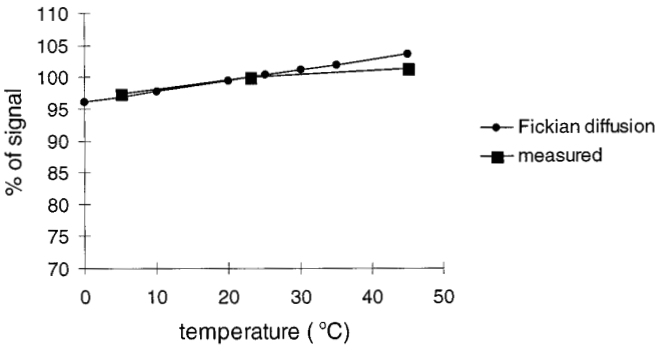


**Figure 4. Temperature influence on the sensitivity. Calculated values in case of Fickian diffusion and measured values for the current sensor. The sensor response at room temperature (23 °C) is defined as 100 %.**


**Figure 5. Carbon monoxide sensor and battery operated alarm device.**

In the fabrication process the most difficult step is the deposition of the Teflon bonded platinum black electrode material. Further improvement of the formulation in combination with development of a printing process is under investigation.

## Conclusions

The sensor architecture presented here, greatly simplifies the sensor fabrication. This presents a first step towards mass production of amperometric carbon monoxide sensors.

The developed sensor functions very well with a detection limit in the sub ppm region. The temperature influence on the sensitivity was remarkably low, so temperature compensation is not necessary. Moreover, the sensitivity was observed to be very stable during the test period of three years thus enabling measurements without recalibration.

Finally, in figure 5 a photograph is given, showing the developed sensor and dedicated electronics, together forming a battery operated carbon monoxide alarm device. This device was developed as a demonstrator during the course of the work presented here.

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