Novel Carbon Monoxide Sensor for PEM Fuel Cell Systems

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ABSTRACT

Research has been conducted to develop a novel sensor for the detection of carbon monoxide in the presence of hydrogen and nitrogen. The automotive fuel cell application requires a sensor to detect low levels of carbon monoxide (~1ppm CO) in order to control the fuel processor. The novel sensing approach pursued here is based on the reversible adsorption of CO onto and complexation with a copper chloride film. When suitable film synthesis conditions are used, the resistance of the device exhibited a rapid and reversible sensitivity to carbon monoxide, even in the presence of 50vol% hydrogen.

INTRODUCTION

The importance of carbon monoxide sensors for automotive PEM fuel cell systems is illustrated by a schematic of an automotive fuel processor, shown in Figure 1. Fuel processing typically involves three or four stages. The first reforming step involves the reaction of gasified hydrocarbons with air (partial oxidation), or with air and steam (autothermal reforming or ATR), to convert gasoline, methanol or other hydrocarbons into a gas mixture rich in hydrogen and carbon monoxide. This reformed gas mixture is then subjected to the water-gas-shift (WGS) reaction to reduce carbon monoxide levels and increase hydrogen content. After exiting the WGS reactors, the hydrogen-rich reformate enters the preferential oxidation reactor (PROX) where the gas is mixed air to oxidize remaining carbon monoxide to carbon dioxide.

The primary use of the CO sensors would be to measure the CO content of the reformate gas exiting the PROX reactor. There are two potential benefits of this type of sensor:

1) The sensor can provide feedback to the PROX reactor to add the appropriate amount of air to oxidize the CO (without sacrificing hydrogen).

2) The sensor will protect the PEM fuel cell stack; detection of CO is extremely important because too much CO will poison the anode catalyst of the PEM fuel cell.

Existing CO sensors are either too expensive or are not selective to CO in reducing environments. Commercial CO sensors based on semiconducting ceramic oxides [1] or solid-electrolytes [2], operate on the basis of a resistance or EMF change due to combustion of CO to CO₂. This type of sensor cannot work for the fuel cell application because of the absence of oxygen in the reformate gas.

The sensing approach described in this work is based on the change in electrical resistance that occurs when carbon monoxide is selectively absorbed by thick film of copper chloride. The choice of copper chloride as a sensing material is based on some previously reported work on copper chloride based adsorbents [3-4]. The CO adsorption mechanism is based on the formation of copper carbonyl chloride via the reaction [3]:

CuCl + CO → Cu(CO)Cl    (1)

The work by Lee [4], is especially pertinent, since they showed that copper chloride based adsorbents selectively adsorb carbon monoxide in reformate gas streams.

EXPERIMENTAL SECTION

The design of our CO sensor is based on a planar device. The sensing platform consists of an alumina substrate with gold interdigital electrodes (IDE). A copper chloride film that is sensitive to the presence of carbon monoxide is deposited as a coating onto the electrodes. When the sensor is operating at an appropriate (and constant) temperature, the magnitude of the resistance measured between the interdigital electrodes provides a measure of the carbon monoxide content of the gas stream. Several approaches were evaluated to prepare thick films of copper chloride sensor material. Two methods of thick film deposition based on the evaporation of copper chloride films from acetonitrile solutions, showed sensitivity to CO.
Copper chloride (97% CuCl, Alfa Aesar) was purified by re-crystallization in hydrochloric acid, followed by washing in acetic acid. In the first method, CuCl was first dissolved in acetonitrile, with nitrogen bubbling through the solution. An IDE substrate was placed on a hot plate and heated to a temperature above the boiling point of acetonitrile (82°C). The CuCl solution was added drop-wise to the hot IDE, allowing the acetonitrile to evaporate, leaving a CuCl film. The drops were added until reasonable film thickness was obtained.

The second approach involved submerging an IDE-alumina substrate in the CuCl/acetonitrile solution. The beaker was placed in a vacuum oven at room temperature to evaporate the acetonitrile. During the removal of the acetonitrile, the CuCl physically precipitated onto the IDE substrate. The sample was vacuum-dried until all solvent was removed. Films prepared by both methods were characterized by x-ray diffraction, scanning electron microscopy and by electrical measurements.

Sensor testing was conducted using the measurement apparatus in Figure 2.

![Testing apparatus for electrical measurement on sensor samples.](image)

A digital multimeter connected via serial port to a computer for controlled data acquisition and digital mass flow controllers were utilized to make electrical measurements and control the sensor environment, respectively.

**RESULTS AND DISCUSSION**

**Characterization of Sensor Materials**

**X-Ray Diffraction**

X-ray diffraction (Scintag Pad V Diffractometer) was utilized to determine if the variations in synthesis methods impacted crystallinity or composition of the CuCl sensor materials. Samples for XRD analyses were prepared by the following methods:

- Purified CuCl powder was dissolved in acetonitrile and mounted onto sample holder directly via drop-wise method.
- Purified CuCl was dissolved in acetonitrile while bubbling N₂ through the acetonitrile. The solution was then added to the sample holder and acetonitrile evaporated in a vacuum oven.

X-ray diffraction data are presented in Figure 3. All samples exhibited the nantokite structure of CuCl.

**Scanning Electron Microscopy**

The microstructures of film samples prepared from CuCl/acetonitrile solutions were evaluated by scanning electron microscopy (see Fig. 4 and 5). Very striking differences in the morphology of the two samples were observed. The sample prepared by dropwise addition of the acetonitrile onto a heated substrate exhibited a highly porous structure of spherical copper chloride particles, whereas the film sample produced by direct precipitation of copper chloride during evaporation of acetonitrile exhibited a lamellar/herring-bone structure; the lamellae comprised of very small spherical copper chloride crystals. These different film morphologies resulted in very different CO sensing behavior, as discussed in the next section. Variations in sensitivity (and selectivity) to carbon monoxide due to surface modifications have also been exhibited in tin-oxide based sensors modified via superacid species [5].
Electrical Measurements

Two point DC electrical resistance measurements were made on the copper chloride processed via drop-wise addition on the IDE and samples fabricated by physical precipitation. The sensor was placed in a 50/50 vol% H$_2$/N$_2$ mixture flowing at 100sccm flow rate. The hydrogen content was changed from 40 to 60 vol% with no change in the baseline resistance. Sensors fabricated via the drop-wise technique while showing a response to CO exhibited low sensitivity (~2%, $\Delta R/R_0$). This could be attributed to surface morphology and lower binding sites for CO complexation. The CO sensing performance of a CuCl film sample prepared by direct precipitation of CuCl by evaporation of acetonitrile solutions is shown in Fig. 7.

The CuCl based sensor shown above shows a fast repeatable response in the presence of 5000ppm CO in hydrogen/nitrogen background at 50°C. The resistance is seen to decrease in the presence of CO and recovers to the initial baseline upon removal of CO. The response to CO is present over many cycles and days as shown in Figure 8.

![Fig. 5 SEM micrograph of copper chloride film prepared via the drop-wise route.](image5)

![Fig. 6 SEM micrograph of copper chloride deposited by physical precipitation.](image6)

![Fig. 7 CuCl thick film response to 5000ppm CO in 50/50 (v/v) H$_2$/N$_2$ gas mixture.](image7)

![Fig. 8 CuCl thick film response to 5000ppm CO after four days of operation.](image8)
hours of operation and numerous cycling. The sensitivity of the sensors fabricated by this route exhibited higher sensitivities than those fabricated via the drop-wise method (~15% vs. 2%). The copper chloride sensor also exhibited a very fast response upon introduction of 5000ppm CO as shown in Figure 9.

Figure 9 shows that the copper chloride based sensors have very fast response times. To obtain a more accurate measurement of the sensor response time, faster data acquisition will need to be employed. The maximum sensitivity to carbon monoxide is between 50 and 60°C. Sensitivities as low as 4ppm CO have been obtained in dry-syngas (N₂/H₂/CO₂/CH₄) environments and these results will be reported in a subsequent publication. When the temperature is increased to greater than 75°C, all sensitivity to carbon monoxide is lost. Also, when testing in humidified nitrogen/hydrogen mixtures all sensitivity to CO is lost. This is interpreted as irreversible oxidation of CuCl in the presence of water-vapor.

A mechanism based upon the formation of a copper carbanal complex was invoked as a possible scheme for sensing CO. However, based on the rapid response and reversibility of CuCl response to CO, it is highly unlikely that the Cu(CO)Cl complex is being formed. Therefore, another model of CO sensing behavior must be explored. This suggestion is supported by the recent literature, specifically from a group in France [6] that has been developing ammonia sensors based on thin films of copper bromide. These workers reported that strong interactions exist at gas-solid interface between surface copper ions and certain gas molecules (e.g. NH₃). Because CuCl is an ionic solid with Frenkel type defects [7], these interactions result in formation of a fixed surface layer of Cu⁺ ions, according to the defect reaction:

\[ \text{Cu}_\text{Cu} + V_S \leftrightarrow \text{Cu}^+ + V^-'_\text{Cu} \]  

where \( V_S \) and \( \text{Cu}^+ \) are an empty surface site and a copper ion at a surface site, respectively. The copper vacancies are distributed in the adjacent space charge region. The net positive charge of the \( \text{Cu}^+ \) would thus be counterbalanced by a negatively charged region enriched in copper vacancies. This mechanism would predict an increase of copper vacancies and thus a reduction of resistance as observed in our work.

**CONCLUSIONS**

The feasibility of using CuCl as a selective CO sensor in the presence of 50vol% hydrogen has been demonstrated. The CO sensing performance of copper chloride films is very sensitive to the synthesis and fabrication methods used. CuCl sensors exhibit very fast response times (~1s), which is fast enough for the fuel cell protection application. Work needs to be pursued to increase the operating temperature of the material to >100°C and improve sensitivity to CO in the presence of water vapor.

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**REFERENCES**