

# Carbon monoxide sensor for PEM fuel cell systems

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## Abstract

Power generation systems based on Proton-exchange membrane (PEM) fuel cells require sensors to detect carbon monoxide to extremely low levels (~1 ppm) in the presence of hydrogen and other gaseous components (nitrogen, carbon dioxide, methane and steam). The CO sensors capable of working in reducing environments are almost non-existent. Development of a new CO sensor stable in H<sub>2</sub>-rich environment is described. The novel sensing approach is based on the adsorption of CO onto a film of an inorganic material that allows CO detection by monitoring resistance changes of the film in a simulated reformed gas, rich in H<sub>2</sub>. When suitable materials were used for the thick film approach, the resistance of the device exhibited a rapid and reversible sensitivity to carbon monoxide in the range 0–5000 ppm over a period of several days, in the presence of hydrogen and nitrogen.

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## 1. Introduction

The use of hydrocarbon fuels for generating power for cars and homes is expected to continue well into the 21st century. Increases in the efficiency of power generation will allow us to reduce our dependence on foreign sources of fuels, while reductions in emissions of greenhouse gases and other pollutants will protect our environment. Fuel cell technology has been identified as a promising path towards achieving these goals. Proton-exchange membrane (PEM) fuel cells are being developed for both transportation and residential power systems. PEM fuel cells operate on hydrogen. However, the infrastructure for hydrogen that will support large markets is decades away. The use of hydrocarbon fuels (e.g. gasoline, natural gas, propane, etc.) in fuel cells requires that these fuels are first converted (or reformed) into a hydrogen-rich gas with little or no carbon monoxide—since even trace levels of carbon monoxide can lead to poisoning of platinum electrocatalysts used in the fuel cells [1,2]. The reforming process involves multiple catalytic reactors, as shown in Fig. 1. In the first step, hydrocarbons are converted to hydrogen and carbon monoxide by reactions with air (partial oxidation), with water

(steam reforming) or with air and water (autothermal reforming). In the second step, carbon monoxide is reduced and hydrogen content increased by subjecting the gas mixture to a water gas shift (WGS) reaction. In the third step, the gas mixture is reacted with air over a preferential oxidation (PROX) catalyst, so the remaining CO is oxidized to CO<sub>2</sub> (hopefully with minimal oxidation of hydrogen). Such fuel processors have been developed to the prototype demonstration stage [3–5].

In a PEM-based fuel cell, knowledge of the CO concentration after the various reaction stages is of paramount importance to any PEM-based power generation systems. For example, CO sensors would provide two primary benefits:

- (1) The sensor can provide feedback to the PROX reactor; this will allow an optimum and regulated air-feed into the PROX reactor (and minimize any wasted hydrogen).
- (2) The sensor will protect the PEM fuel cell stack; when a high CO content is detected the reformat gas would be diverted from the stack (with power being provided by a battery) until the CO level returns to tolerable levels.

Existing carbon monoxide sensors cannot meet the requirements of the PEM fuel cell system. Commercial CO sensors, typically based on semiconducting oxides (e.g. tin oxide), operate on the basis of a resistance change

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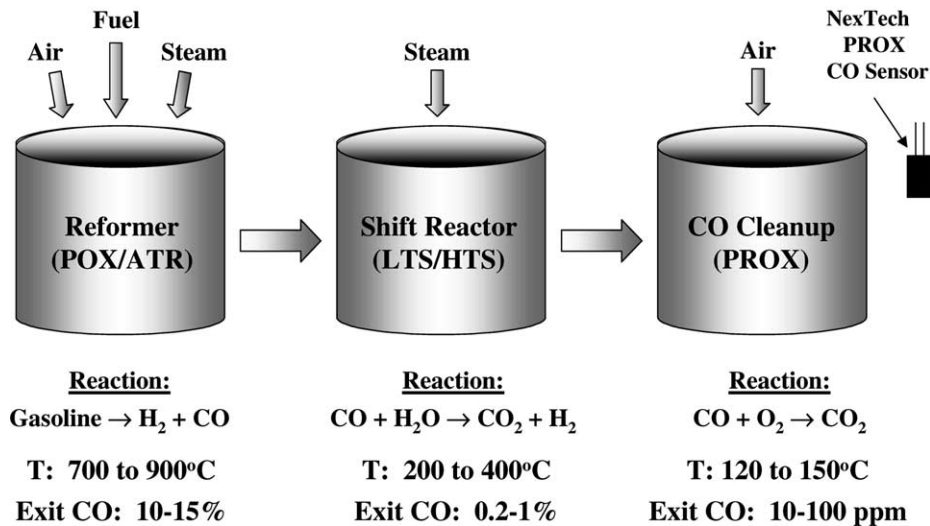


Fig. 1. Schematic diagram showing steps in a fuel processor.

due to the chemisorption of oxygen from the ambient and oxidation of CO to  $\text{CO}_2$  [6,7]. This type of sensor cannot work for the fuel cell application because of the absence of oxygen in the reformat gas. We have recently developed a chemical sensor that shows sensitivity to the presence of 1000 ppm carbon monoxide in  $\text{H}_2$ -rich reformed gas background [8]. In this paper, results on the development of a fast responding and durable chemical sensor based on copper(I) chloride thick films sensitive to CO in  $\text{H}_2$ -rich environment are presented. It was found that the method of film preparation and the associated surface morphology had a profound effect on the performance of the film.

## 2. Experimental

Commercial grade copper(I) chloride (97% pure from, Alfa-Aesar, MA) was used to fabricate the CO sensing film. Prior to making the film, as received copper(I) chloride was purified by re-crystallization from concentrated hydrochloric acid, followed by repeated washing with glacial acetic acid. Several approaches were evaluated to prepare thick films of the sensor material. The design of CO sensor is

based on a planar device. The sensing platform consisted of an alumina substrate printed with gold inter-digitated electrodes (IDE) in a comb-teeth format. Copper chloride film was deposited as a coating onto the electrodes. Two methods of thick film deposition based on the evaporation of copper chloride films from acetonitrile solutions were employed. In the first method, about  $\sim 75$  mg CuCl was dissolved in 4 ml of the organic solvent, with nitrogen bubbling through the solution. An IDE substrate was placed on a hot plate and heated to a temperature in the vicinity of the boiling point of acetonitrile ( $82^\circ\text{C}$ ). The CuCl solution was quickly added drop-wise to the hot IDE, allowing the solution to spread and solvent to evaporate, leaving a CuCl film. The drops were added until a reasonable film thickness was achieved. 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 solvent. During the solvent removal, CuCl physically precipitated onto the IDE substrate. The sample was vacuum-dried until all of the solvent was removed. The structural and microstructural features of the films prepared by both the methods were investigated via X-ray diffraction (Scintag Pad V Diffractometer) and scanning electron

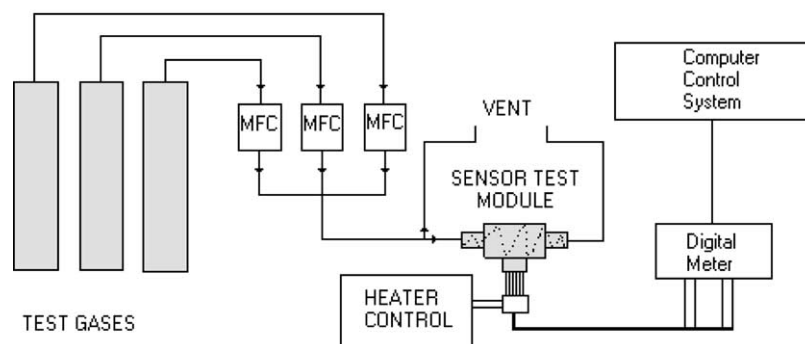


Fig. 2. Testing apparatus for electrical measurements on CO sensors.

microscopy (XL-30 FEG), respectively. Samples for XRD analyses were prepared by the following methods:

- Purified CuCl powder was dissolved in acetonitrile and mounted onto the sample holder directly via drop-wise method.
- Purified CuCl was dissolved in acetonitrile while bubbling N<sub>2</sub> through the acetonitrile. The solution was then added to the sample holder and evaporated in a vacuum oven.

Sensor testing was conducted using the apparatus shown in Fig. 2.

The sensor was enclosed in a 1.5 in. diameter stainless steel T-joint with the help of gas-tight Swagelok fittings, which was externally heated by means of a heating tape wound on the stainless joint and controlled (within  $\pm 1^\circ$ ) through a temperature controller. The Swagelok T-joint provided a practical gas volume to do the response time testing. An Agilent (model 34401) 6.5 digit multimeter interfaced via serial port to a desktop computer was utilized to make electrical measurements. The HP 34812 Benchlink software was used for automated data acquisition.

### 3. Results and discussion

#### 3.1. Structural and microstructural characterization of the sensor material

The XRD patterns obtained on the sensor films derived via two fabrication methods are shown in Fig. 3. Identical diffractograms are suggestive of the fact that the original nantokite structure of CuCl (ICDD 6-0344) was retained in both the films irrespective of the way they were prepared.

On the other hand, striking differences in the morphology of the two samples were observed. The sample prepared by

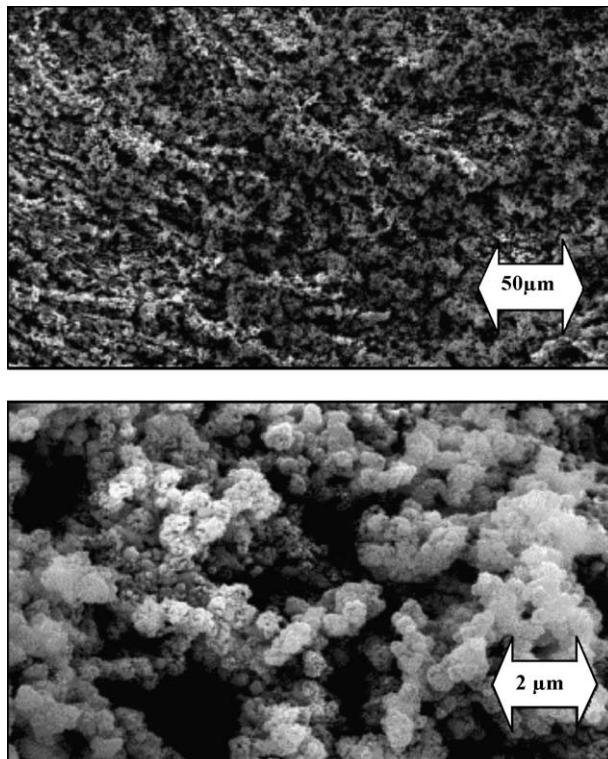


Fig. 4. SEM micrograph of copper chloride film prepared via “drop evaporation” route.

drop-wise addition of the CuCl/CH<sub>3</sub>CN solution onto a heated substrate exhibited a highly porous structure consisting of spherical agglomerated copper chloride particles (Fig. 4), whereas the film produced by direct precipitation of copper chloride via solvent evaporation, exhibited a lamellar/herringbone structure (Fig. 5). The high magnification micrograph (Fig. 5b) shows that the lamellae in fact comprised of very small copper chloride crystals having spherical morphology.

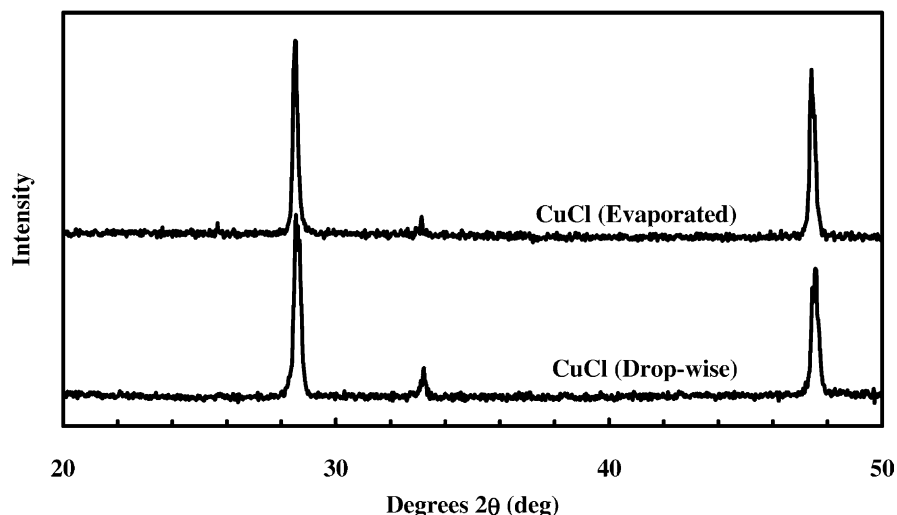
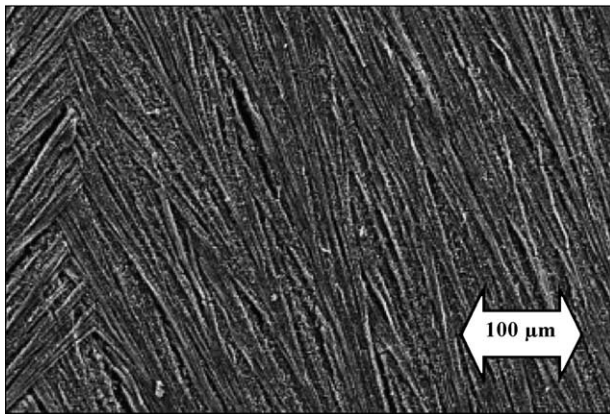
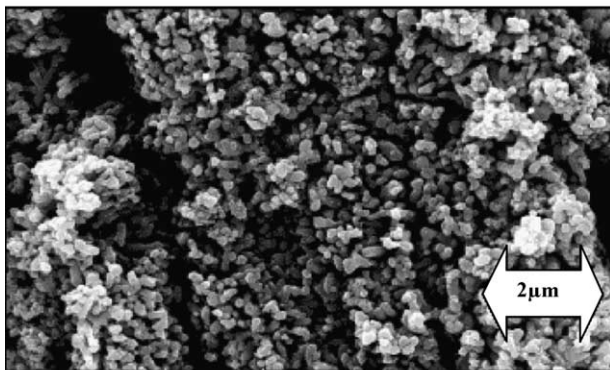


Fig. 3. XRD patterns of the CuCl films fabricated by two techniques.



(a)



(b)

Fig. 5. SEM micrograph of copper chloride film deposited by physical precipitation.

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 [9].

### 3.2. Electrical measurements

Two-point dc electrical resistance measurements were made on the film processed via drop-wise addition on the IDE as well as on the samples fabricated by physical precipitation. The sensor was first conditioned in pure nitrogen as temperature was slowly raised to  $\sim 50^\circ\text{C}$  to obtain a steady baseline resistance. High purity hydrogen was blended so as to obtain a 50/50 (v/v)  $\text{H}_2/\text{N}_2$  mixture flowing at 100 sccm flow. After a quick and small initial dip, the baseline was restored. This is a significant result since it indicates that the film resistance was immune to the presence of as high as 50 vol.%  $\text{H}_2$  in the ambient. The hydrogen content was varied between 40 and 60 (v/v) with no change in the baseline resistance.

Upon introduction of 5000 ppm of CO, sensors fabricated via the drop-wise technique showed a response to CO albeit with low sensitivity ( $\Delta R/R_0 \sim 2\%$ , where  $R_0$  is the resistance of the film in 50/50  $\text{N}_2/\text{H}_2$  mixture). This could be attributed to the evolved surface morphology (reduction in surface area) and correspondingly fewer sites for CO surface adsorption and complexation [10–14]. On the other hand, films prepared via physical evaporation in vacuum were found to exhibit higher sensitivity to CO. The CO sensing performance of a CuCl film sample obtained by direct precipitation of CuCl through evaporation of acetonitrile solution in vacuum is shown in Fig. 6.

As can be readily seen, the sensor shows a fast and repeatable response in the presence of 5000 ppm CO in hydrogen/nitrogen background at  $50^\circ\text{C}$ . The resistance is seen to decrease in the presence of CO and recovers to the initial baseline upon removal of CO. The behavior is consistent over many cycles and several days as shown in Fig. 7. There is only a slight drift in the baseline (approximately 3%) after the fourth day of cycling. Fig. 8 shows that the CuCl is stable in the hydrogen/nitrogen atmospheres and

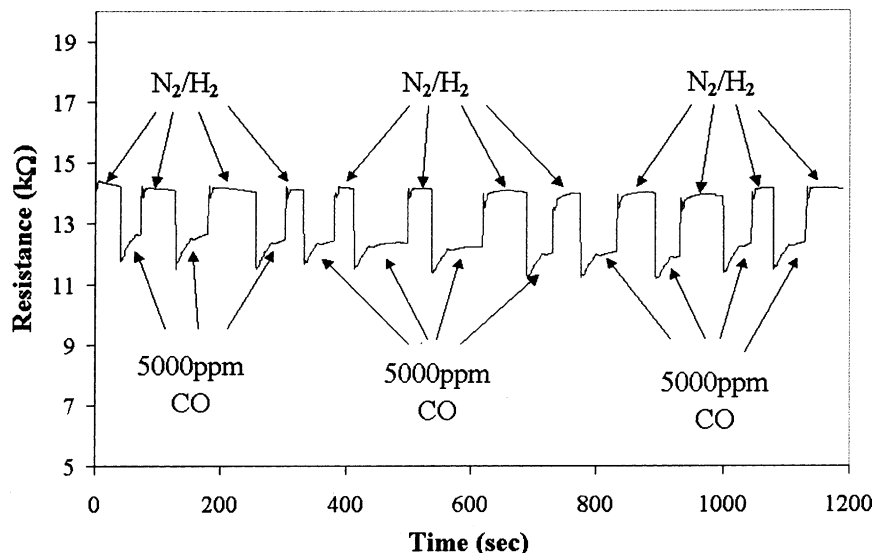


Fig. 6. CuCl thick film response to 5000 ppm CO in a 50/50  $\text{H}_2/\text{N}_2$  mixture.

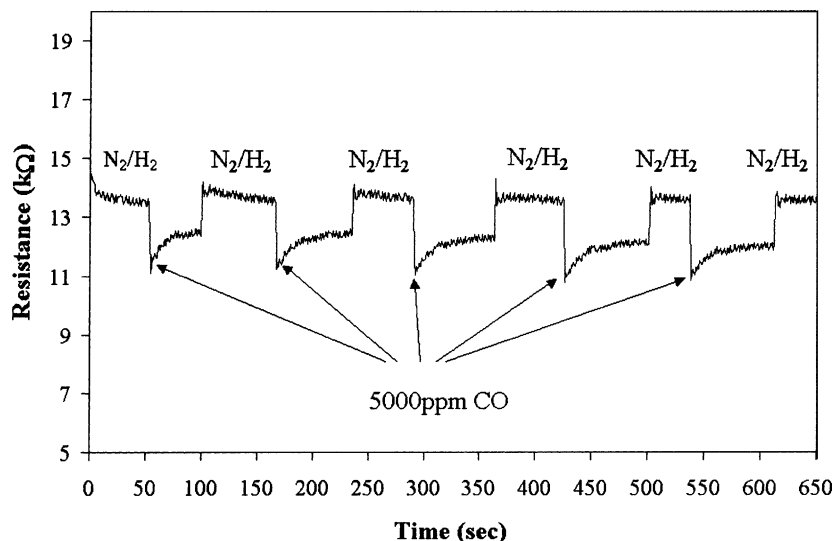


Fig. 7. CuCl sensor response after 4 days of testing.

exhibits no reduction even after 100 h of cycling. The additional peaks have been identified as alumina and gold from the underlying inter-digitated electrode substrate.

A desirable characteristic of a successful chemical sensor is its ability to respond to the change in chemical environment in its vicinity as quickly as possible. Accordingly, the copper chloride sensor exhibited a very fast response upon introduction of 5000 ppm CO as shown in Fig. 9. The  $t_{90}$  is less than 1 s.

The maximum sensitivity to carbon monoxide was observed between 50 and 60 °C. When the temperature was raised to  $\geq 75$  °C, all sensitivity to CO was lost. Also, when testing in humidified nitrogen/hydrogen mixtures, all sensitivity to CO is lost. The loss in CO sensitivity is interpreted as hydration of the sensor films in the presence of water vapor, which impedes CO complexation. After testing in humidified environments the films were found to be slightly green and upon further examination via XRD

the single phase CuCl was partially converted to two new phases. Fig. 10 shows the slight conversion of the sensor films to  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ .

The decrease in resistance upon introduction of CO is consistent with a mechanism invoked previously [8]. We proposed a hole conduction mechanism for CO sensing on CuCl films. Formation of  $\text{Cu}^{2+}$  on the surface by oxidation during film preparation appeared to be a critical step. This was noted as a grayish/white colored film after deposition. One mechanism to generate holes would be from the non-stoichiometry ( $\text{Cu}_{1-x}\text{Cl}$ ) in the CuCl film. The defect chemistry for this non-stoichiometry suggests that copper vacancies are the majority defects and these can ionize to give holes. Electronic hole conduction was found to be the dominant conduction mechanism for CuX (X = Cl, Br) films made by evaporation and was explained by the formation of Cu(II) during the evaporation process [15]. We believe that it is this presence of Cu(II) on the surface that impedes hole

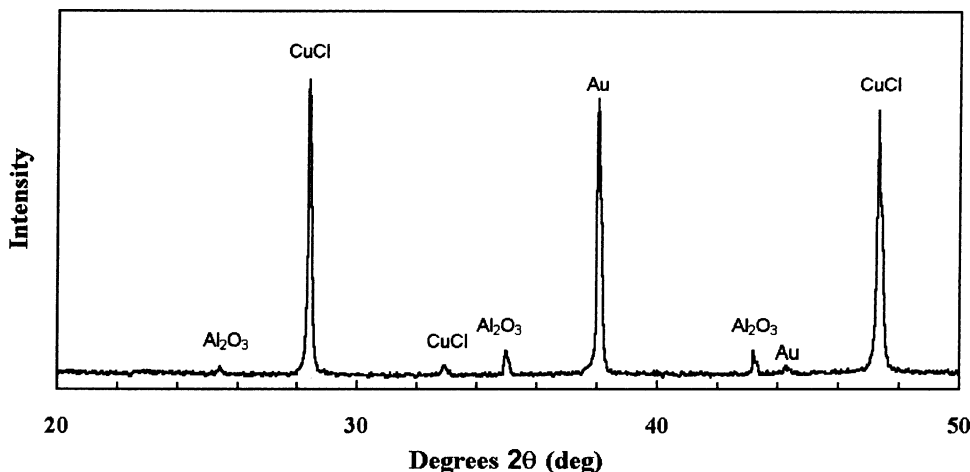


Fig. 8. XRD pattern of the CuCl sensor after 4 days of testing.

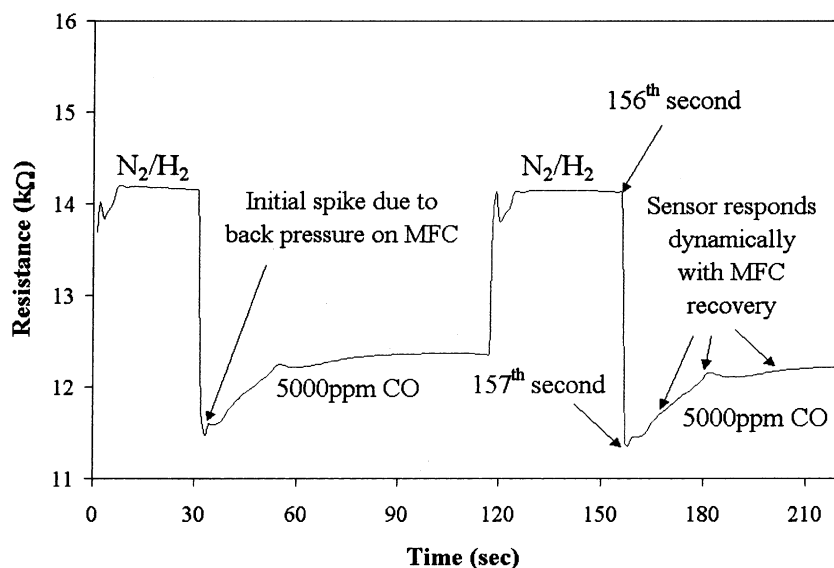


Fig. 9. Thick film sensor exhibiting very fast response time ( $\sim 1$  s).

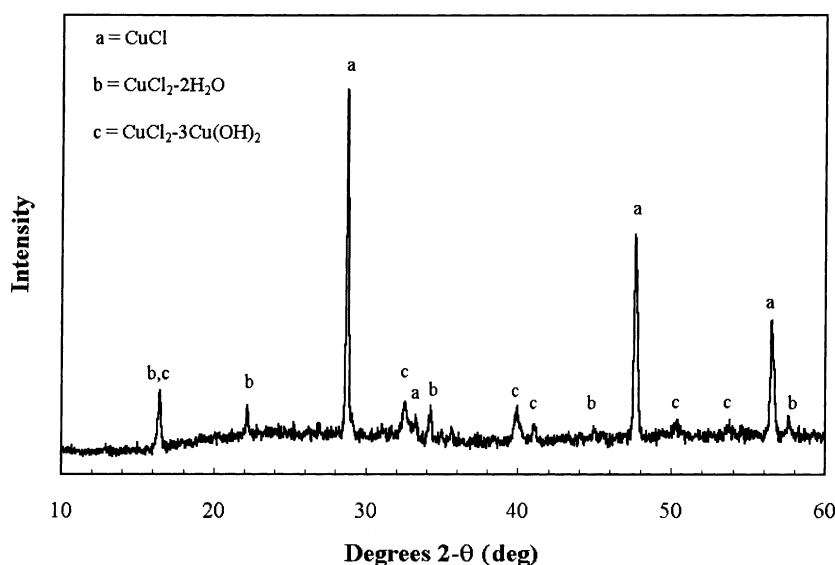


Fig. 10. XRD showing slight conversion of the sensor films to hydrated copper chloride.

migration between CuCl grains. However, upon introduction of CO, the coordination complex  $\text{Cu}(\text{CO})\text{Cl}$  is formed, resulting in a loss of the barrier due to Cu(II). The fast response times also lead to the hypothesis that a surface controlled mechanism is controlling the response.

#### 4. Conclusions

The feasibility of using CuCl as a selective CO sensor in the presence of 50 vol.% 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 ( $\sim 1$  s), which

is fast enough for the fuel cell protection application. The CO sensor has a repeatable response to hydrogen over many cycles with minimal drift in the baseline resistance. The presence of water vapors in the gas stream was found to be extremely deleterious to the operation of these sensors. Further work needs to be done to evaluate the cross-sensitivity to other syngas species (i.e.  $\text{H}_2\text{S}$ ) and to improve CuCl film integrity in the presence of water vapor.

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