

# Detection of CO in a reducing, hydrous environment using CuBr as electrolyte

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## Abstract

The resistance changes of CuBr upon exposure to carbon monoxide (CO) are explored as the sensing principle in this study. X-ray diffraction and thermal analysis were used to characterize the CuBr. Thick-films of CuBr deposited on an alumina substrate with gold interdigitated electrodes were used as the sensing element. Interaction with CO led to decrease in electrical resistance of the films. The presence of H<sub>2</sub> in the background gas did not influence the resistance. Humidity, on the other hand did change the background resistance, but at constant humidity, the sensor exhibited resistance changes with CO. This sensor could be useful for CO detection in the hydrated environment of polymeric-based fuel cell systems that use hydrocarbons.

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## 1. Introduction

There is need for sensors for rapid monitoring of carbon monoxide (CO) concentrations in process gas streams. Of particular interest is the gas stream in polymer electrode membrane fuel cell (PEMFC) fuel cells, where, upon reforming hydrocarbon fuels, small amounts of CO are present even after the water-gas shift reaction. Trace amounts of CO in the reformed gas poison the Pt electrodes and the cell performance is degraded [1,2]. The typical semiconductor-based sensors (SnO<sub>2</sub> or TiO<sub>2</sub>) cannot be used in the reducing environment present in the anodic compartment typical of fuel cells, and new strategies for sensing is required [3–5].

We have recently reported on sensors based on the reversible complex-forming reactions of CO with Cu(I) chloride [6,7]. Even though these sensors showed promise for CO sensing in reducing environments (H<sub>2</sub>), the presence of water vapor led to complete loss of sensitivity. In this paper, we are reporting the results of a CuBr-based CO sensor that can operate in a reducing environment and constant water vapor.

Large number of studies has been done on the electronic conductivity of copper(I) bromide [8,9]. At temperatures

above 300 °C, ionic conductivity is predominant, though electronic-hole conductivity is manifested at lower temperatures. Knauth and coworkers have reported extensively on the use of sputtered CuBr films for sensing of ammonia [10–13]. The use of Lewis acid–base complex as the basis for sensing was also demonstrated for NH<sub>3</sub> on silver halide films [14,15].

## 2. Experimental

Commercially available CuBr (99.999% from Aldrich) was used as a precursor. Pastes of CuBr with proper rheology were prepared by mixing with an organic medium using acetonitrile (HPLC grade). The paste was coated with a brush onto Al<sub>2</sub>O<sub>3</sub> substrates that had screen-printed interdigitated Au electrodes. The thickness of the sensor film was about 60 μm.

The sensor was heated in flowing N<sub>2</sub> and H<sub>2</sub> gas mixture at various temperatures in the range 100–300 °C for 2 h. The sensing experiments were performed within a quartz tube located inside a tube furnace. The resistance of the sensor was monitored by a Hewlett Packard multimeter attached to a computer-controlled characterization system (Benchlink software was used). The sensor performance was tested in gas mixtures containing 50% H<sub>2</sub>, 100–2000 ppm CO with N<sub>2</sub> (ppm = milligram per kilogram) as the carrier gas in dry and wet streams. The gases were metered through mass flow

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controllers to form mixtures of various compositions with a gas flow kept constant at 100 cm<sup>3</sup>/min. The sensor films were also characterized by powder diffraction (XRD) and thermal (DTA/TGA) methods before and after exposure to CO.

### 3. Results and discussion

#### 3.1. Characterization of CuBr

Fig. 1 shows the X-ray diffraction patterns of the thick film of CuBr used in this study. All the peaks agree with assignment to  $\gamma$ -CuBr, as reported in JCPDS data file (06–292).

Fig. 2 shows the TGA/DTA curves of CuBr. The weight loss at  $\sim 480^\circ\text{C}$  can be associated with the melting of the sample. The DTA profile shows sharp endothermic peaks at 389.7, 468.4 and 487.7  $^\circ\text{C}$  characteristic for transitions from  $\gamma \rightarrow \beta$ ,  $\beta \rightarrow \alpha$  and melting, respectively, and is characteristic of CuBr [16].

#### 3.2. Optimization of sensor

The sensitivity is calculated as the ratio of the resistance of the sensor in test gas containing CO ( $R_g$ ) to the resistance in the background  $\text{H}_2/\text{N}_2$  gas ( $R_a$ ). The resistance measure-

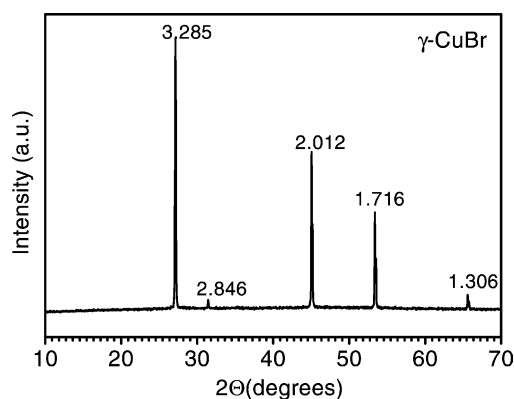


Fig. 1. Powder X-ray diffraction pattern of a CuBr thick film.

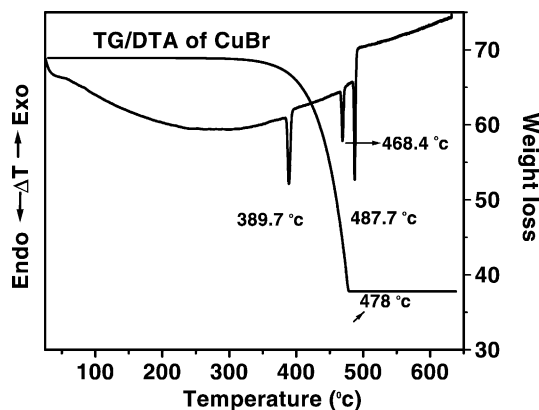


Fig. 2. TGA/DTA data of CuBr. Absolute weight of the sample is plotted on the right-hand axis (starting weight = 68.75 mg).

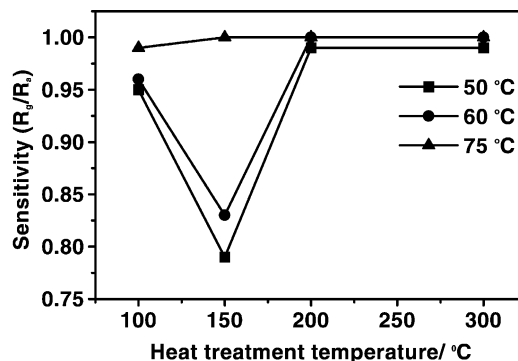


Fig. 3. Response characteristics ( $R_g/R_a$ ) of CuBr sensors heat treated to different temperatures to 1000 ppm CO in  $\text{N}_2/\text{H}_2$  background. Sensor operating temperatures, 50–75  $^\circ\text{C}$  ( $R_g$ : resistance in  $\text{CO}/\text{N}_2/\text{H}_2$ ,  $R_a$ : resistance in  $\text{N}_2/\text{H}_2$ ).

ments were made with Au interdigitated electrodes. We examined the dependence of the thermal treatment of CuBr on the sensitivity. Heating was carried out at temperatures ranging from 100 to 300  $^\circ\text{C}$  for 2–4 h. All samples showed no change in resistance upon exposure to  $\text{H}_2$ , as had been observed before for CuCl [6].

Fig. 3 shows the sensitivity versus heat treatment temperature of CuBr upon exposure to 1000 ppm CO gas at different sensing temperatures in the presence of  $\text{H}_2/\text{N}_2$ . These data suggest that the maximum sensitivity value is obtained for samples heated at 150  $^\circ\text{C}$  for 2 h. Also, the best sensitivity is observed at sensor operating temperature of 50  $^\circ\text{C}$ . Thus, all the experiments reported below were done with samples prepared under these conditions. There was no change in the DTA thermogram before and after sensing (identical to Fig. 2), showing that the CuBr remains in the  $\gamma$  phase after sample preparation and sensing.

#### 3.3. Sensor performance

Fig. 4 shows the change in CuBr sensor resistance with dry CO in a background of  $\text{H}_2/\text{N}_2$  at 50  $^\circ\text{C}$ . The time axis is plotted in minutes. The response ( $\tau_{\text{res}}$ ) and recovery ( $\tau_{\text{rec}}$ ) times (defined as the time taken to reach 90% of the response when gas is introduced or removed) was  $\sim 30$  s for response and  $\sim 60$  s for recovery. These response times depend on the gas flow rates. Reproducible signals were obtained with CO concentrations as low as 100 ppm.

For fuel cell applications, besides the reducing atmosphere, another important consideration is that the sensor be able to function in the presence of humidity. We examined the effect of humidity by bubbling gases through water prior to exposure to the sensor. Fig. 5 shows the change in resistance as the dry gas is replaced by wet gas (all for reducing background) for a CuCl sample. It is clear that the sensor performs in the dry gases, but that the resistance drops precipitously in the presence of water. The baseline varied with time, and no response to CO was observed. Fig. 6 shows the resistance profile upon introduction of water over a CuBr

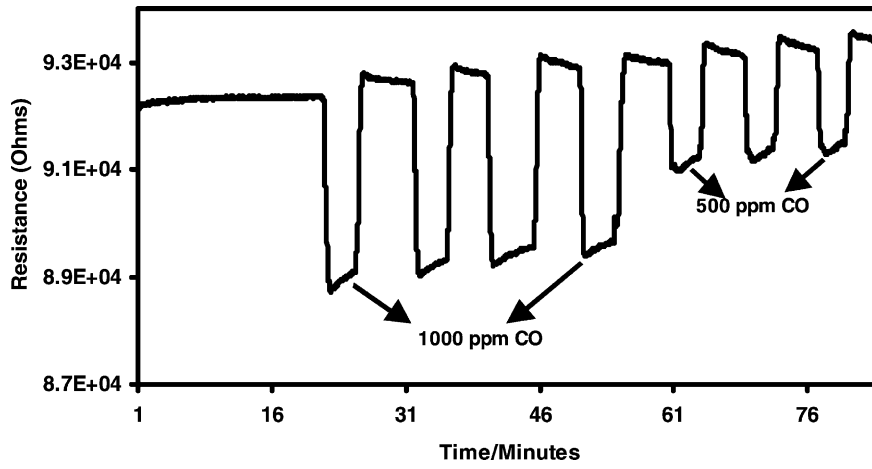


Fig. 4. Resistance of CuBr at different concentrations of CO in a background of H<sub>2</sub>/N<sub>2</sub> at 50 °C.

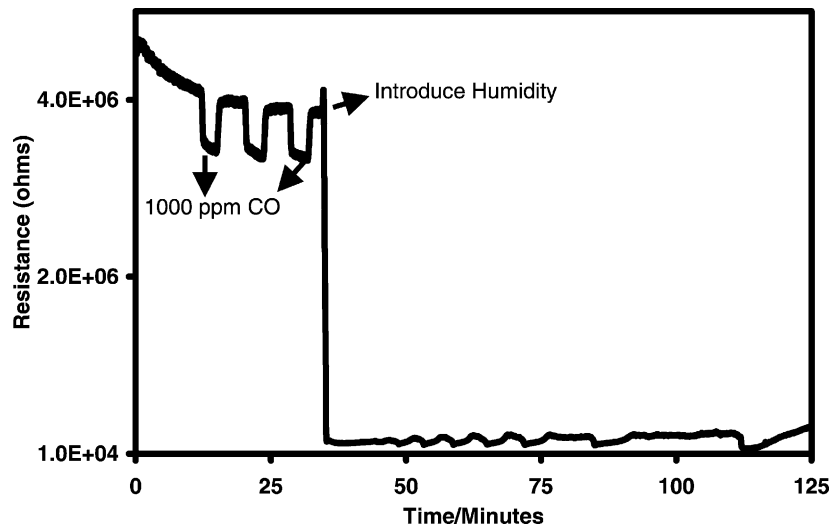


Fig. 5. Resistance of CuCl in dry 1000 ppm CO and upon exposure to humidity at 50 °C (background gas: H<sub>2</sub>/N<sub>2</sub>).

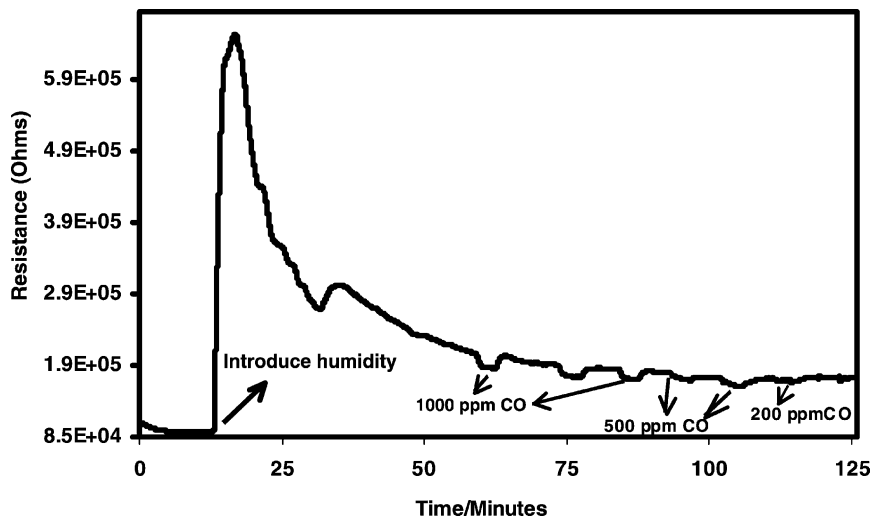


Fig. 6. Resistance change of CuBr upon exposure to humidity and CO at 50 °C (background gas: H<sub>2</sub>/N<sub>2</sub>).

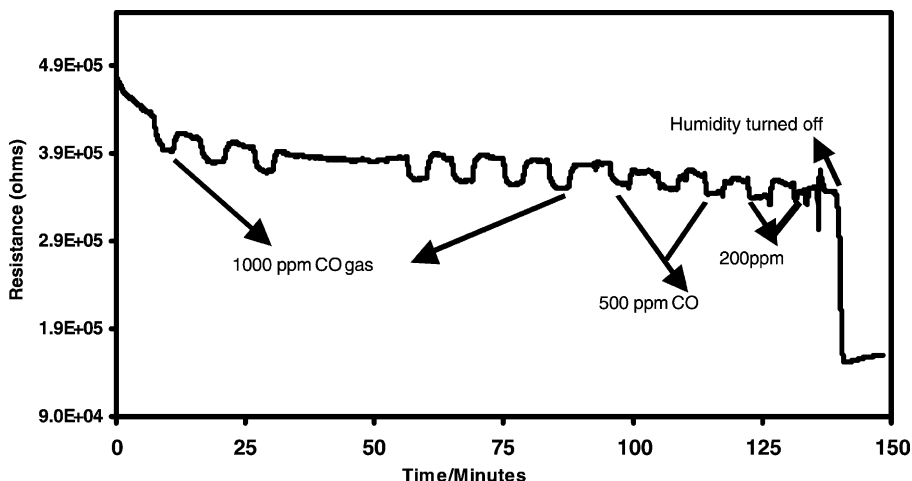


Fig. 7. Resistance change of CuBr upon exposure to CO at 50°C under humid conditions (background gas: H<sub>2</sub>/N<sub>2</sub>).

sample. There is an immediate increase in the baseline resistance, which decays over several hours to a stable value. During this changing background, CO was introduced and resistance changes could be clearly observed. More importantly, after the CuBr sensor has stabilized in the presence of water, sensing of CO could be readily done as shown in Fig. 7. However, as also shown in Fig. 7, if the humidity is turned off and dry gases are introduced, then the background again drops. Thus, this sensor can perform as long as the humidity in the background is kept constant. Fig. 8 compares the sensor response to varying concentrations of CO in dry and wet gas streams. The sensitivity is lower in humid environment than in the dry gas. The response and recovery times are also longer.

We have discussed the basic mechanisms of copper halide sensing for CO in an earlier paper and similar mechanism should hold for CuBr [6]. Considering the temperatures of operation, the interaction of CO is restricted to surface of the halide in both cases. The relevant issue of discussion here is why CuBr can act as a sensor in humidity and CuCl does not. Because of our use of Au electrodes, only the electronic conductivity of CuBr is of interest [8,9]. The origin of the

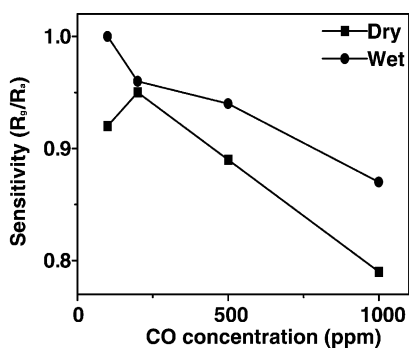


Fig. 8. Comparison of response characteristics ( $R_g/R_a$ ) of a CuBr sensor to CO in dry and wet conditions (background gas: N<sub>2</sub>/H<sub>2</sub>, operating temperature: 50°C,  $R_g$ : resistance in CO/N<sub>2</sub>/H<sub>2</sub>,  $R_a$ : resistance in N<sub>2</sub>/H<sub>2</sub>).

p-type conductivity can arise from both copper deficiencies and/or oxygen doping [17]. In both CuCl and CuBr, the binding of CO in the form of Cu(CO)X is expected to occur. For X = Cl, this compound has been isolated and consists of chloride-bridged layers with CO bound to the tetrahedrally coordinated Cu(I) [18]. There is no structural information available on the CuBr analog, except it has been noted that the reaction of CO with CuBr occurs to a much lesser extent than CuCl, and CuI is thought to be unreactive towards CO [19]. We find that the sensitivity of CuCl sensors towards CO is better than that of CuBr (compare Fig. 3 with Fig. 1d in [6]), presumably due to the better coordination by CO in the case of CuCl.

The solubility of CuCl and CuBr in water is  $1.1 \times 10^{-3}$  and  $2.0 \times 10^{-4}$  M, respectively [20]. We propose that it is the lower solubility of CuBr that makes it possible for this material to function in a hydrous environment. CuBr is known to be less hygroscopic, and recently it has been found to be preferable to CuCl for water-activated batteries because loss of copper ions by oxidation and dissolution is markedly less as compared to the chloride [21]. The solubility of CuI in water is the lowest of all three halides ( $2.2 \times 10^{-6}$  M), but its inability to complex CO makes it impractical to use as a sensor material.

There is, however, a marked difference in the resistance of CuCl and CuBr upon exposure to humidity, which is not readily explained and is the subject of ongoing investigation.

#### 4. Conclusions

This paper demonstrates that CuBr-based sensor has potential for CO detection in wet, reducing environments. The sensor can detect CO above 100 ppm at an optimum operating temperature of ~50°C. These copper halide based sensors are attractive materials for detection of CO in a H<sub>2</sub> environment, where semiconductor oxide based sensors do

not perform. Further optimization will require operation at higher temperatures, if it is to be used in a fuel cell environment.

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