A Downhole CO₂ Sensor to Monitor CO₂ Movement In Situ for Geologic Carbon Storage

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Abstract

This paper describes how a downhole CO₂ chemical sensor was prepared for use in determining the concentration of CO₂ in water, particularly in harsh, high-pressure environments such as those found in geological formations considered for the geologic storage of CO₂. The sensor consisted of a pair of Ir/IrO_x and Ag/AgCl electrodes, a gas-permeable membrane, a bicarbonate-based internal electrolyte solution, and porous stainless steel as supporting material. The sensor was tested in the solution with different concentrations of CO₂ and displayed very good CO₂ sensing performance under pressures of 1000, 2000, and 3000 psi. A linear relationship between the sensor response potential and the logarithm of the CO₂ concentration was obtained for the sensor under different pressures. Reproducibility of the sensor was examined and the results indicated that the sensor displayed excellent reproducibility. CO₂/brine core flooding tests were carried out to evaluate the performance of the CO₂ sensor in simulate CO₂ storage process. The results indicated that the sensor could detect CO₂ movement in the tests. Further studies showed that the sensor could be reused by brine flooding after CO₂/brine flushed the core. The results of the core flooding tests demonstrated that the sensor had potential application for CO₂ monitoring in carbon storage.

Keywords: CO₂ sensor; CO₂ monitoring; Carbon storage

Introduction

Geologic storage of carbon dioxide (CO₂) has been proposed as a viable means for reducing anthropogenic CO₂ emissions^[1-5]. The means for geological storage of CO₂ is injection of supercritical CO₂ at storage depths, which requires the CO₂ to remain either supercritical, or in solution in the water/brine present in the formation storing the CO₂. For example, at Sleipner, Norway, millions of tonnes CO₂ were reported to have been injected into the storage formation

with depth of ~1000 meters, storage pressure of 1,725 psi and temperature of 46°C.^[6] However, there are aspects of geologic storage that need further study, particularly in regards to security. To date, no current geologic storage locations have been tested as a commercial-scale CO₂ storage site for very large amounts of CO₂ storage. Establishing environmental security and addressing public concerns require widespread monitoring of the process in the deep subsurface. In addition, studies of subsurface carbon storage such as flow simulations, models of stored CO₂ reactions and transports require a comprehensive monitoring process to accurately characterize and understand the storage process.

Real-time information about stored CO₂ movement and concentration change is highly helpful for: (1) better understanding the uncertainties present in CO₂ geologic storage; (2) improvement of simulation models; and (3) evaluation of the feasibility of geologic CO₂ storage. Current methods to monitor stored CO₂ include seismic,^[7] geoelectric,^[8] isotope and tracer methods,^[9-11] and fluid sampling analysis.^[12,13] However, these methods commonly result in low resolution, high cost, and the inability to monitor continuously, in real time, over the long time scales of the CO₂ storage process. A preferred way of monitoring in-situ CO₂ migration is to directly employ CO₂ sensors at storage depth. Such a sensor must be able to resist harsh environmental conditions such as high pressure and high brine salinity.

A number of studies have proposed various types of CO₂ sensors.^[14-17] John and Joseph^[15] disclosed a planar bicarbonate sensor that, combined with a pH sensor, could measure the concentration of CO₂ in water. However, the high pressures prevalent underground prevented the sensor from working correctly under such conditions. Maier^[16] et al. reported a CO₂ sensor that might work at high pressure. But the disadvantage of their sensor is that it cannot work in high humidity; that is, when CO₂ is dissolved in water, as in geological CO₂ storage. Recently, fiber optic sensors have been reported to monitor CO₂ in high pressure environments.^[18-20] By measuring the wavelength shift of polystyrene coated long-period gratings, Melo et al.^[18,19] demonstrated that a FOS based LPG could monitor dissolution of CO₂ in water under high pressure. Lin and Lou^[20] developed a localized surface plasmon resonance fiber-optic probe to determine the refractive indices of supercritical CO₂ (scCO₂) and scCO₂-ethanol mixtures. However, such fiber optic sensors had significant correlation to pressure,^[17,18] which obstructs the application of these sensors in CO₂ storage.

This paper describes a suitable CO₂ chemical sensor that can monitor CO₂ concentration change at storage depth in real time. The working principle of the developed CO₂ sensor is based on the measurement of the pH change of the sensor's internal electrolyte solution, caused by the hydrolysis of CO₂. It is known that, as CO₂ dissolves in water, the following equilibrium occurs:

According to the Nernstian equation, the output potential of the pH electrodes can be written as:

$$E = E_0 + \frac{2.303RT}{F} \log[H^+] \quad (2)$$

where E_0 is the standard electrode potential (mV). R is the universal gas constant: $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$. T is the temperature in kelvin, and F is the Faraday constant, $F = 96.5 \text{ mC mol}^{-1}$. At standard temperature (25°C), equation (1) can be written as:

$$E = E_0 + 59.15 \log[H^+] \quad (3)$$

As CO_2 dissolves in the solution, equilibrium occurs according to equation (1) and the following equation can be obtained:

$$E = E_0 + 59.15 \log \frac{k}{[\text{HCO}_3^-]} + 59.15 \log[\text{CO}_2] \quad (4)$$

where k is the equilibrium constant. The internal electrolyte is composed of bicarbonate salt, which has a high concentration of bicarbonate compared to the bicarbonate from CO_2 dissociation. Then $59.15 \log \frac{k}{[\text{HCO}_3^-]}$ can be regarded as a constant. Equation (4) then becomes:

$$\Delta E = E - E'_0 = 59.15 \log[\text{CO}_2] \quad (5)$$

Hence, the CO_2 concentration can be determined through measuring the change in output potential. In CO_2 geological storage operations, CO_2 is injected into formations such as deep saline or depleted oil reservoirs. An equilibrium between the injected CO_2 and the formation brine exists in the front zone where the CO_2 plume contacts with formation brine. The proposed CO_2 sensor can monitor the CO_2 concentration change in the brine and determine the CO_2 plume movement in carbon storage. In addition, water-alternating-gas (WAG) has been widely applied currently for CO_2 storage and enhanced oil recovery. During the WAG operation, water and gas (CO_2) slugs are alternatively injected into formation reservoir. This requires the developed CO_2 sensor can be regenerated and reusable in WAG CO_2 storage. In this study, a downhole CO_2 sensor is developed and prepared. Then the sensor is tested under different high pressures. Bench-scale experiments of CO_2 /brine core flooding are performed to evaluate the performance of the CO_2 sensor in a simulated CO_2 storage process.

Experimental

Construction of the CO_2 sensor: A Severinghaus-type CO_2 sensor^[21,22] was prepared for detection of CO_2 at storage depth. The sensor consisted of a pair of electrodes, a gas-permeable membrane, a bicarbonate-based internal electrolyte solution, and support materials. Figure 1 shows the schematic structure and picture of the fabricated CO_2 sensor. The inside of the electrodes,

working electrode Ir/IrO_x and reference electrode Ag/AgCl, were prepared as described by Yao.^[23] Iridium wires (20 mm in length) were first cleaned with 6 M HCl and then with deionized (DI) water. The cleaned wires were placed in an aluminum crucible and covered with Li₂CO₃ powder. The crucible was then put in an electric furnace and the furnace temperature was set at 870°C for 5 h under air conditions. After it cooled down to room temperature, the crucible was rinsed with diluted HCl to remove the solid carbonate. The oxidized iridium wires were cleaned with DI water and dried overnight at 120°C. The Ag/AgCl reference electrode was prepared by chloridizing the surface of a silver wire. The chloridization of the silver wires was performed in a solution containing 1 M FeCl₃–0.1 M HCl for 24 h. After that, the wire was rinsed with DI water and put in a saturated AgCl solution for 24 h. Then the wire was dried at 120°C overnight and ready for preparation of the CO₂ sensor. To prepare the CO₂ sensor, the inside of a porous stainless steel cup was coated with silicon membrane to prevent internal solution corrosion. Gas-permeable silicone tubing was wrapped around the porous cup and the bottom side of the cup was sealed with silicone sealant (Fig. 1). The prepared Ir/IrO_x and Ag/AgCl electrodes were connected with gold wire and silver wire, respectively. Both the gold wire and silver wire were wrapped with plastic film to prevent contact with each other. Then the two electrodes were positioned parallel in the porous stainless steel cup with the two connected wires, gold and silver wires, coming out through the two separated cap holes. The cup was filled with a prepared 0.01M NaHCO₃–0.1 M NaCl solution and then covered with the cap and sealed with silicone sealant. The CO₂ sensor, after preparation, was 1.0 in. in diameter and 2.5 in. in length. Finally, the prepared CO₂ sensor unit was stored in a 0.01M NaHCO₃–0.1 M NaCl solution.

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Test of the performance of the CO₂ sensor under different pressures

The performance of the CO₂ sensor was tested by the following procedure. All potentiometric measurements were carried out at standard temperature of 25°C±2°C. Figure 2 shows the schematic drawing of the experiment setup. The CO₂ sensor was first placed in a stainless steel tank. The tank was filled with 0.2M citric acid and sealed tightly at both ends. The connecting wires of the sensor emerged from one end of the tank. The other end connected an ISCO pump with 0.375 in. stainless steel tubing. Two valves were located between the stainless steel tank and the ISCO pump. Valve 1 controlled the pump injection and valve 2 controlled the tank pressure. A pressure meter was installed between the tank and valve 2. The meter was used for monitoring the tank pressure during the test. Before the tests were performed, a certain volume of 0.1M NaHCO₃ solution was injected into the tank and the tank was immediately sealed. Then the pump

was started, increasing the tank pressure. When the stainless steel tank pressure reached the desired pressure (1,000 psi, 2,000psi, and 3,000 psi, respectively), valve 2 was closed to keep the pressure constant. The sensor output signal was measured by a 34401A 61/2 digital multimeter. The CO₂ concentration of the solution was increased by addition of NaHCO₃ solution. Under acidic conditions, all bicarbonate and carbonate were converted into CO₂, so the CO₂ concentration could be calculated from the added amount of the NaHCO₃. Once the CO₂ molecule was formed in the sample solution, it diffused through the gas-permeable membrane into the internal solution of the CO₂ sensor until equilibrium was reached. The CO₂ dynamic range of 10⁻⁴ M to 10⁻² M were able to be established in this way. Concentrations of CO₂ higher than 10⁻² M exhibited a fast loss of CO₂, so that the CO₂ concentration continuously decreased.^[14] Therefore, each CO₂ concentration was made fresh and used immediately.

CO₂/brine core flooding test

Core flooding is a technique used for conducting experiments on core samples in conditions simulated to be as close to the natural environment as possible. A core flooding system was constructed to simulate the CO₂ storage process and evaluate the performance of the CO₂ sensor in the process. Figure 3 shows the schematic diagram of the core flooding apparatus. Two ISCO syringe pumps (model 260D) were used to inject brine (2.0% NaCl) and liquid CO₂ into a sandstone core sample. Two floating piston accumulators were used to reserve brine and high-pressure liquid CO₂, respectively. Three TEMCO backpressure regulators (BPR) were used to maintain the required operation pressure. A core sample purchased from Cleveland Quarries was wrapped with a layer of lead foil. After that, the lead foil-covered core was inserted into a rubber core sleeve and mounted in the coreholder with an overburden pressure of 3500 psi. The use of a rubber core sleeve prevented the water supplying the overburden pressure to diffuse into the core. The prepared CO₂ sensor was inserted into the end of the core as shown in Fig. 3b. Two wires of the sensor exited the coreholder through a high-pressure connector. The entire apparatus, except for syringe pumps, was placed in an air bath to maintain a constant temperature throughout the experiment.

Reservoir core characterization indicated that sandstone and limestone are suitable for CO₂ storage.^[24-26] In addition, the goals of CO₂ storage process are to put a large quantity of CO₂ into the subsurface and keep it there for a long time, which requires the CO₂ storage formation to have adequate permeability, for example, several hundred million-Darcy.^[25, 27] In this study, a sandstone core was used in CO₂/brine core flooding tests to simulate the CO₂ storage process and

evaluate the CO₂ sensor performance. The properties of the core sample are listed in Table 1.

Results and Discussion

1, Response characteristics of the CO₂ sensor

The IrO_x electrode displayed pH sensitivity.^[28] The CO₂ sensor prepared with IrO_x electrode was tested under 2,000 psi pressure. Figure 4 displays the potential response of CO₂ sensor during the test. At the beginning, the output potential of the sensor was stabilized at ~70.4 mV. Then, as the NaHCO₃ was added into the citric acid solution, CO₂ was formed in the solution and it began to diffuse into the internal electrolyte of the CO₂ sensor, resulting in the pH change of the internal electrolyte. The output signal of the CO₂ sensor stayed at ~70.4 mV for 40 min. then started to increase after NaHCO₃ was added into the solution. This delayed sensor response contributed to diffusion of the CO₂ molecules in the silicon membrane. Once the CO₂ molecules reached the internal solution, the output potential of the sensor started to increase. Figure 4 indicates that the output potential increased to 147.8 mV and then leveled off, implying an equilibrium obtained between the generated CO₂ and the internal solution.

Figure 5 illustrates the sensitivity curves of the CO₂ sensor at standard temperature and 2,000 psi. The linear relationship between the sensor response potential differential and the logarithm of the CO₂ concentration is quite good in the tested range of 0.001M to 0.006M. The slope of the line is 107.5 mV/Log [CO₂], which is larger than the theory value of 59.15 mV/Log [CO₂], indicating super-Nernstian behavior occurred.^[29] Here, it is necessary to point out that, in the real CO₂ storage process, the CO₂ injection formation has different formation fluid composition and temperature. However, because the CO₂ sensing probes (IrO_x and Ag/AgCl electrodes) are located inside the sensor chamber and the sensor's inside electrolyte is separated from the outside formation fluid by the gas permeable membrane, it is expected that different formation fluids would have no effect on the sensor performance for CO₂ monitoring. On the other hand, formation temperature might affect the sensor response according to equation 3. For example, if the formation temperature is 37°C instead of standard temperature, equation 3 becomes $E = E_0 + 61.50 \log[H^+]$. The slope of the sensor response curve increases a little. Hence, the sensor needs to be calibrated at the formation temperature.

2, The performance of the CO₂ sensor under different pressures

During the CO₂ storage process, supercritical CO₂ is injected into geologic formations under high pressure, so the effect of high pressure on the performance of the CO₂ sensor was important to evaluate. The typical formation pressures for CO₂ storage are in the range of 1,000 ps–4,000 psi, in which most of the formation pressures are around 2,000 psi.^[30] Therefore, the performance of the CO₂ sensor was tested under pressures of 1,000 psi–3,000 psi in this study. Figure 6 illustrates the results of the CO₂ sensor response under different pressures. The results indicate that linear interrelationships between the sensor output potential change and log[CO₂] are obtained under all the tested pressures. In addition, few deviations were observed for the sensor under different pressures, indicating the CO₂ sensor can work under high pressures without changing its performance. This is important for subsurface CO₂ monitoring because all geologic CO₂ storage is initiated under the formation pressure and the formation pressure is expected to increase as more CO₂ is injected into the formation reservoir.

Reproducibility of the CO₂ sensor was examined by testing the sensor in CO₂ solution three times. The sensor was first equilibrated in different concentrations of dissolved CO₂ solution under 2,000 psi. Then, it was removed from the solution and immersed into a fresh solution (no dissolved CO₂) for seven days. After that, the sensor was placed in a similar dissolved CO₂ solution again and the potential change was measured. This cycle was repeated several times to evaluate the reproducibility of the sensor. Figure 7 displays the results of the CO₂ sensor in solution with CO₂ concentration of 0.001M under 2,000 psi. The results indicate that the prepared CO₂ sensor exhibited good reproducibility during the tests. The potential changes for the three tests were 20.9 mV, 19.7 mV, and 19.4 mV, respectively. A little shift of the potential was observed after the sensor was removed from the fresh solution, indicating some residual CO₂ remained in the internal solution and did not escape from the solution in seven days.

3, Monitor CO₂ migration in simulated CO₂ storage process

Bench-scale core flooding experiments were performed to evaluate the performance of the CO₂ sensor in subsurface CO₂ storage process. A sandstone core was used to simulate the process of CO₂ storage in a sandstone saline aquifer. After the sensor was loaded in the core, the core flooding test was initiated by injection of 2.0% brine into the core with flow rate of 100 ml/hr.

The injection pressure of the core was around 1,500 psi. One pore volume (PV) of brine was injected into the core to saturate the core with brine, which is similar to initial CO₂ storage saline aquifer conditions, as the formation rock is saturated with brine. Then CO₂/brine was injected into the core with the phase ratio of CO₂/brine = 1:1 and total flow rate = 100 ml/hr. The response of the CO₂ sensor during this process was recorded as shown in Fig. 8.

The results demonstrate that, when 2.0% brine was injected into the core, the output signal of the sensor was around 75.6 mV. The output signal stayed constant as 1 PV of brine flooded the core, indicating that the sensor was equilibrated with ambient conditions. Then, when CO₂ began injection into the core, the output potential was the same as that in the brine flooding test for almost 42 minutes and then it suddenly increased to ~264.1 mV. Apparently, as CO₂ injection was initiated, CO₂ moved forward along the core and took ~35 minutes to reach the sensor. The output potential of the sensor stayed unchanged before the CO₂ plume arrived. When the injected CO₂ reached the sensor, the CO₂ molecule diffused into the sensor and changed the pH of the internal solution, resulting in an immediate potential increase to 264.1 mV. The response time of the sensor, due to the high pressure and concentration of the CO₂, was around 17 minutes. After that, the output potential leveled off, implying new equilibrium was reached in the sensor's internal solution. The change of the output potential, based on the results of Fig. 8, is ~188.5 mV. The higher potential change compared with the results in Fig. 7 indicates that, instead of dissolved CO₂, a pure CO₂ plume reached the sensor. However, in the real process of CO₂ storage, the injected CO₂ displaces the brine in the formation reservoir. There will be a front zone in which some of the injected CO₂ dissolves in the brine. The front zone is located in front of the CO₂ plume and moves forward with the injected CO₂. The CO₂ sensor would first contact and detect the front zone with a slow potential increase and then a sudden increase as CO₂ plume arrives.

A second CO₂/brine core flooding test was performed with the CO₂ sensor. This procedure was similar to the first test, except that the sensor was flooded with brine after the CO₂/brine core flooding. Figure 9 shows the result of the sensor output potential change during the test. The sensor output potential was around 61.3 mV during the brine flooding. Then the output potential started to slowly increase after 0.5 PV of CO₂/brine was injected into the core, indicating some dissolved CO₂ diffused into the sensor as discussed above. After that, as ~1 PV of CO₂/brine was

injected into the core, an abrupt potential increase was observed. This high potential increase indicated the CO₂ plume reached the sensor, as shown in Fig. 8. Then after the sensor is equilibrated with the CO₂ plume, the core switches to brine flooding. The result indicates that, after ~7 PV brine flooded the core, the sensor recovered almost to its initial state (the output potential was ~70.1 mV and initial output potential was ~61.3 mV). This implies that our downhole CO₂ sensor can be recovered by brine flooding in CO₂ storage process. This is promising for the sensor application in WAG CO₂ storage operation. However, further tests need to be conducted to understand the sensor performance and lifetime in WAG operation.

Conclusions

An electrochemical downhole CO₂ sensor was developed that provided CO₂ sensing performance under pressures of 1000, 2000, and 3000 psi for dissolved CO₂ measurement. A linear relationship between the sensor response potential and the logarithm of the CO₂ concentration was obtained for the CO₂ sensor under different pressures. Bench-scale core flooding tests indicated that the sensor could detect CO₂ movement under the estimated reservoir conditions. Further studies displayed that the sensor could be reused by undergoing brine flooding after CO₂/brine flushes the core. The results of core flooding tests demonstrate that the sensor may have potential application for CO₂ monitoring in carbon storage.

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(a)

(b)

Fig. 1 Schematic structure (a) and picture (b) of the fabricated CO₂ sensor.

Fig. 2 Schematic drawing of the experiment setup.

(3a)

(3b)

Fig. 3 Schematic diagram of the core flooding test (3a); and the diagram of the CO₂ sensor loaded in the core flooding system.

Fig. 4 Potential response of the CO₂ sensor with time in [CO₂] = 0.002 M under 2,000 psi.

Fig. 5 $\text{log}[\text{CO}_2]$ as a function of the potential change under the pressure of 2,000 psi.

Fig. 6 $\text{log}[\text{CO}_2]$ as a function of potential change under different pressures.

Fig. 7 Reproducibility test of the downhole CO₂ sensor in [CO₂] = 0.001M and pressure = 2,000 psi.

Fig. 8 CO₂ sensor potential change during the coreflooding test.

Fig. 9 Results of the CO₂ sensor reproduction in CO₂/brine coreflooding process.

Table 1. Core Properties

Core	Length (cm)	Diameter (cm)	Porosity	Brine Permeability (mD)
Sandstone	24.1	3.8	21.8%	143