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## **Development and Evaluation of an Iridium Oxide Based Chemical Sensor for Downhole CO<sub>2</sub> Monitoring--Part I**

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### **Abstract**

Geological carbon sequestration represents a long-term storage of CO<sub>2</sub>, in which large-scale CO<sub>2</sub> is injected into the subsurface geologic formations, such as the deep saline aquifers or depleted oil and gas reservoir. In the CO<sub>2</sub> sequestration process, the injected CO<sub>2</sub> is expected to remain in the reservoir and not to migrate to the earth surface. To better understand the CO<sub>2</sub> movement undersurface and obtain real time information in carbon sequestration, an iridium oxide-based Severinghaus-type CO<sub>2</sub> chemical sensor was constructed and tested in this study.

The CO<sub>2</sub> sensor was designed and constructed based on the intersection inspiration from electrochemistry idea. The principle of the CO<sub>2</sub> sensor design is dramatically rely on the pH detection of the electrolyte solution which generated by the hydrolysis process of CO<sub>2</sub>. The developed CO<sub>2</sub> sensor includes a couple of Iridium-Oxide electrodes. To meet the working purpose, iridium oxide nanoparticles was prepared and electrodeposited for the thin IrO<sub>2</sub> film generation on the surface of metal substrate. The other critical parts, such as a thin gas-permeable silicone membrane, a porous metal supporting material, and the bicarbonate-based electrolyte solution are prepared for the sensor's preparation. The assembled sensor was tested in aqueous solution with different CO<sub>2</sub> concentrations. Then the sensor was settled in harsh, high-pressure environments, in order to invest the performance of the CO<sub>2</sub> sensor under reservoir conditions.

## Introduction

The definition of CO<sub>2</sub> sequestration was the whole process of the CO<sub>2</sub> capture and the CO<sub>2</sub> long-term storage<sup>[1]</sup>. It had been treated as a potential method to decelerate the accumulation process of greenhouse gas which generated from the fossil fuels burning and other source<sup>[2]</sup>. While for the geologic sequestration, it means to put the captured CO<sub>2</sub> in the geological formation for the aim of long-term storage.

Fig. 1 represents the options for the geological CO<sub>2</sub> storage. Vast amount of formations such as the deep saline aquifers, the depleted oil & gas reservoirs and the coal beds can provide the optical space and seals for the CO<sub>2</sub> trapping in deep underground. Those chosen formations should be deeper than 2600ft and have the good porosity for the large-scale CO<sub>2</sub> storage. Also, the required permeability could permit the large and fast injection rate of CO<sub>2</sub>.

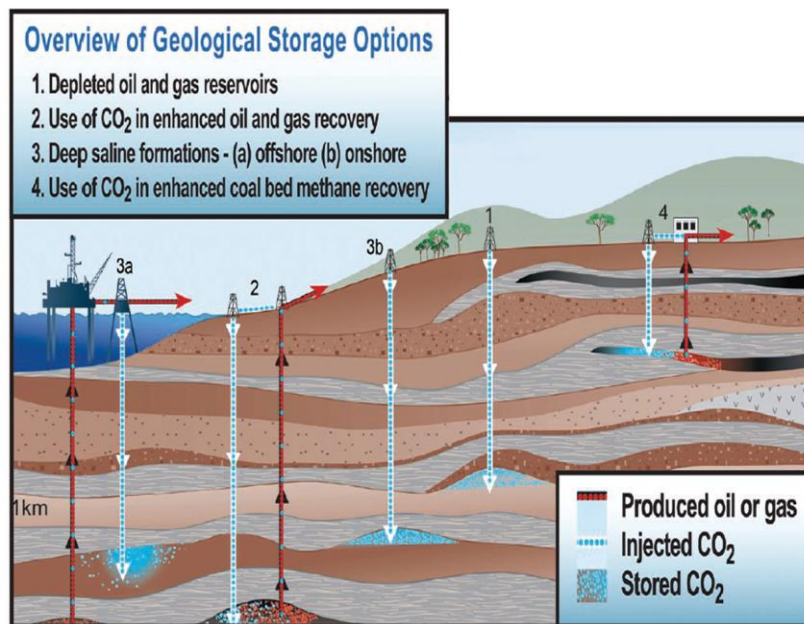


Fig. 1 Styles of geological formations and reservoirs applied for carbon sequestration<sup>[3]</sup>

During the geological CO<sub>2</sub> storage process, the injected CO<sub>2</sub> is expected to stay in the subsurface formations. However, public concerns of CO<sub>2</sub> migration and possible leakage to surface require comprehensive studies and understanding the CO<sub>2</sub> migration behavior in subsurface. An in-situ CO<sub>2</sub> monitoring approach is highly desirable for this purpose.

Comparing with other technologies, which may had largely time consuming or costly requirement, a preferred method for in-situ underground CO<sub>2</sub> migration monitoring is to install down-hole CO<sub>2</sub> sensors directly in the underground. This potential approach may realize by the interaction with the electrochemical idea, which is, transforming the CO<sub>2</sub> detection to the pH measurement<sup>[4]</sup>. At present a great deal of research is carrying out on the CO<sub>2</sub> chemical sensor. For example, in 1998, Trapp *et al.* disclose a coulometric CO<sub>2</sub> gas sensor, which could continuously measure the concentration of CO<sub>2</sub> under atmospheric conditions, but not for the harsh environment such as high pressure, high temperature and high salinity conditions<sup>[5]</sup>. U.S. patent 5554272 revealed a planar

bicarbonate sensor combined with a pH sensor that could detect the CO<sub>2</sub> concentration in the water environment <sup>[6]</sup>. However, the sensor did not work efficiently under the high pressures prevalent underground. The CO<sub>2</sub> sensor developed by Maier *et al.* was reported to work under high pressure condition while not the high humidity circumstance <sup>[7]</sup>.

The purpose of this study is to develop a downhole CO<sub>2</sub> sensor which can be used in carbon sequestration to in situ and continuously monitor CO<sub>2</sub> movement. This study primarily presented the development and test of a robust, novel downhole CO<sub>2</sub> sensor which can monitor CO<sub>2</sub> concentration changes continuously at subsurface condition <sup>[8]</sup>. Differed from the traditional sensor, this type of the CO<sub>2</sub> sensor used a metal-oxide electrode instead of a glass electrode to improve the resistant ability for the harsh downhole environments encountered <sup>[9]</sup>. Up to date, this Severinghaus-type sensor will be the first downhole, chemical CO<sub>2</sub> sensor for monitoring CO<sub>2</sub> movement under simulated reservoir conditions. And that will generate an invaluable effect for large-scale storage of CO<sub>2</sub>. Distinct from all other monitoring methods, this small size chemical sensor is easy to handle and could provide the monitoring data continuously, timely and accurately.

## Experimental

### Sensor preparation

The CO<sub>2</sub> sensor was designed and constructed across the intersection with electrochemistry idea. The principle of the CO<sub>2</sub> sensor design is dramatically based on the pH detection the electrolyte solution which generated by the hydrolysis process of CO<sub>2</sub>. The CO<sub>2</sub> molecules spread through the thin gas-permeable silicone membrane and then dissolve into the internal solution, after that the CO<sub>2</sub> will have a reaction with H<sub>2</sub>O to generate the carbonic acid. While the carbonic acid is not stable, it will dissociate into HCO<sub>3</sub><sup>-</sup> and H<sup>+</sup> (as seen in Equation 1). Consequently, the generated H<sup>+</sup> will vary the pH value of the solution, which is measured through the electrodes.



For the sensor applied under high pressure conditions and simulated reservoir conditions, the construction procedure was described as Fig. 2. Firstly, the working electrode was prepared through the electrodeposition method, in which the iridium oxide nanoparticles solution was electrochemically deposited using cyclic voltammetry onto the metal substrates <sup>[10]</sup>. Then the electrodes were fixed through a stainless steel cap and stabilized by silicone sealant. Following a stain steel porous filter element was settled for the function of supporting the whole frame, which means that it can enable the sensor to work under harsh downhole environment, especially under high pressure condition. This support unit was coated by silicone sealant onto the inner and outer surface in case of contacting with electrodes. What followed is the above stabilized electrodes were inserted into the support unit where inside being full of bicarbonate-based internal electrolyte solution. All the joints were sealed by the silicone sealant in order to preventing the internal solution leakage. Finally, as above mentioned sealing method, both outlets of the gas-permeable membrane were blocked off by the silicone sealant. Meanwhile, some other tiny materials were applied in the sensor manufacture for the purpose of support and potential transfer.

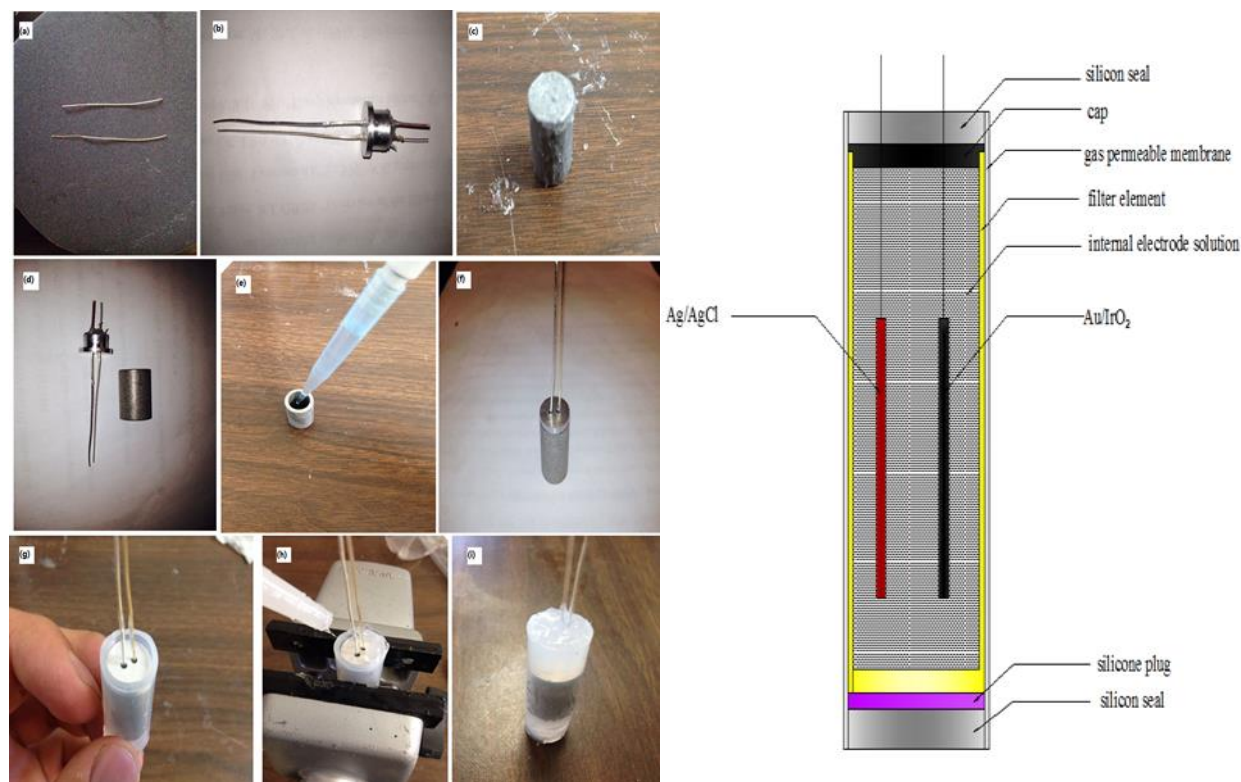


Fig. 2 Construction of CO<sub>2</sub> sensor and schematic of the CO<sub>2</sub> sensor.

### Test of the performance of the CO<sub>2</sub> sensor under different CO<sub>2</sub> concentrations.

The following steps were designed to investigate the CO<sub>2</sub> sensor's performance. All potentiometric measurements were carried out at room temperature of  $25^{\circ}\text{C} \pm 2^{\circ}\text{C}$ .

Fig. 3 shows the schematic figure for setting up the experiment. Firstly, the CO<sub>2</sub> sensor was settled in the stainless steel tank. Then the tank was injected with 0.2M citric acid and tightly sealed. The stainless steel tubing and the connecting wires from the sensor came out from the top of the tank. The ISCO pump was connected with this stainless steel tubing (0.375 in.) and used for controlling the pump injection and the tank pressure. The connecting wires of the sensor were connected with a 34401A 61/2 digit multi-meter. Before carrying out the tests, the base potential of the CO<sub>2</sub> sensor was measured by maintaining the CO<sub>2</sub> sensor into the citric acid solution under a certain pressure. After the potential reached a stable value, the certain amount of the NaHCO<sub>3</sub> solution (0.1M) was injected in the tank and then the tank was sealed immediately. Finally the ESCO pump was began to increase the tank pressure. The sensor output signal was measured by the digit multi-meter. The whole process was conducted under the pressure of 3000psi.

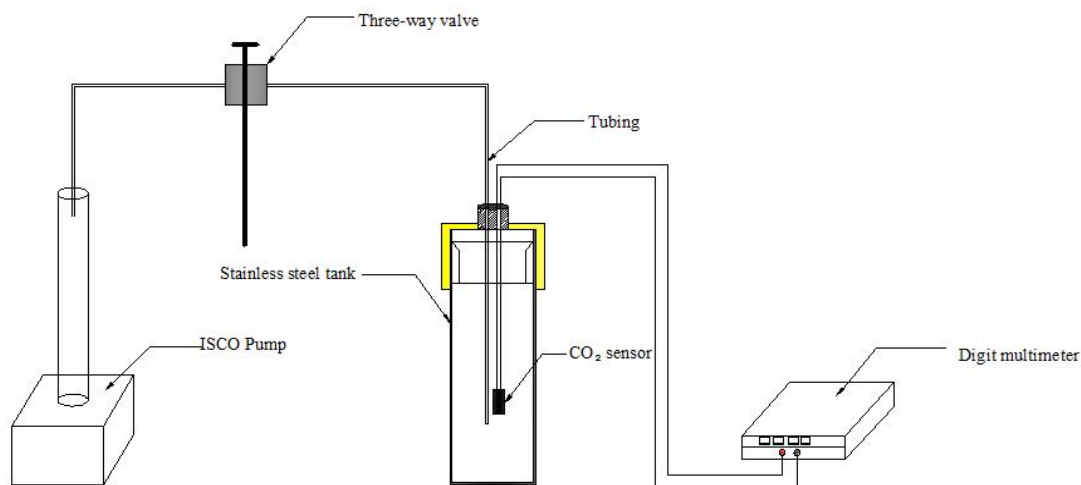


Fig. 3 Schematic structure of the high pressure plant.

### CO<sub>2</sub>/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 coreflooding system was constructed to simulate the CO<sub>2</sub> storage process and evaluate the performance of the CO<sub>2</sub> sensor in the process. Fig. 4 shows the schematic diagram of the core flooding apparatus. Shown in Fig.4, a coreholder mounts the core sample under high overburden pressure, similar to conditions in formations used for underground CO<sub>2</sub> storage. The downhole CO<sub>2</sub> sensor is placed into the core and monitors the CO<sub>2</sub> movement. After CO<sub>2</sub> and brine are filled in two different accumulators and connected with two different backpressure regulators (BPR), the two pumps start to inject distilled water into the accumulator and push CO<sub>2</sub> and brine out from the accumulator. The mixture flows through two filters with pore size of 0.5 μm. Then the CO<sub>2</sub>/brine mixture flows into the core sample where CO<sub>2</sub>/brine contacts with the downhole CO<sub>2</sub> sensor. A change on the output signal of the sensor is used for monitoring the movement of CO<sub>2</sub> and concentration change in the core. In the experiments, the core sample is first flooded with brine to saturate the core. Then liquid CO<sub>2</sub> and brine are injected into the core. After CO<sub>2</sub> and brine emerge from the core, the mixture flows through another BPR, which controls the operation pressure in the core. Then the mixture separates as liquid phase and gas phase after emerging from the BPR. The liquid phase (brine) is collected in a liquid trap and the gas phase (CO<sub>2</sub>) emits to the outside of the building through 0.125 in. tubing. The entire apparatus, except for the pumps, is contained in an air bath box to maintain a constant temperature throughout the experiment.

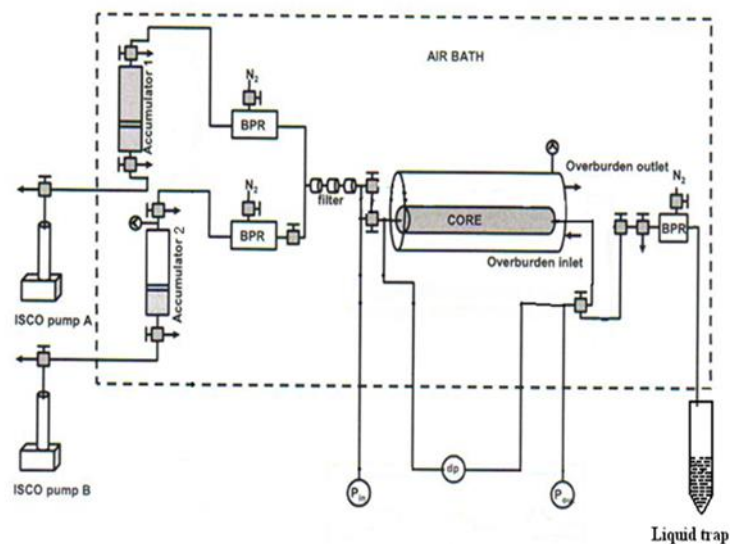


Fig. 4 The schematic diagram and pictures of the core flooding apparatus.

## Results and Discussion

### CO<sub>2</sub> sensor performance test under high pressure (3000 psi)

Response time  $t$  and potential differential  $\Delta E$  are two important parameters to evaluate the CO<sub>2</sub> sensor sensitivity. The potential differential was defined as:  $\Delta E = E(\text{CO}_2) - E(\text{base})$ , the response potential caused by CO<sub>2</sub>. Therefore, the CO<sub>2</sub> responses for each sensor were evaluated by using  $\Delta E$  and response time  $t$  in this experiment.

Figure 5 illustrates a typical potential response of the CO<sub>2</sub> sensor. The measurement was divided into three stages: 1) the potential stabilized at 80 mV in the bicarbonate-based internal electrolyte

solution; 2) the CO<sub>2</sub> diffused through the gas permeable silicone membrane to the internal electrolyte solution. As a result, the potential dramatically increased from 80 mV to 126 mV; 3) the reaction reached the equilibrium and the potential stabilized at 126 mV.

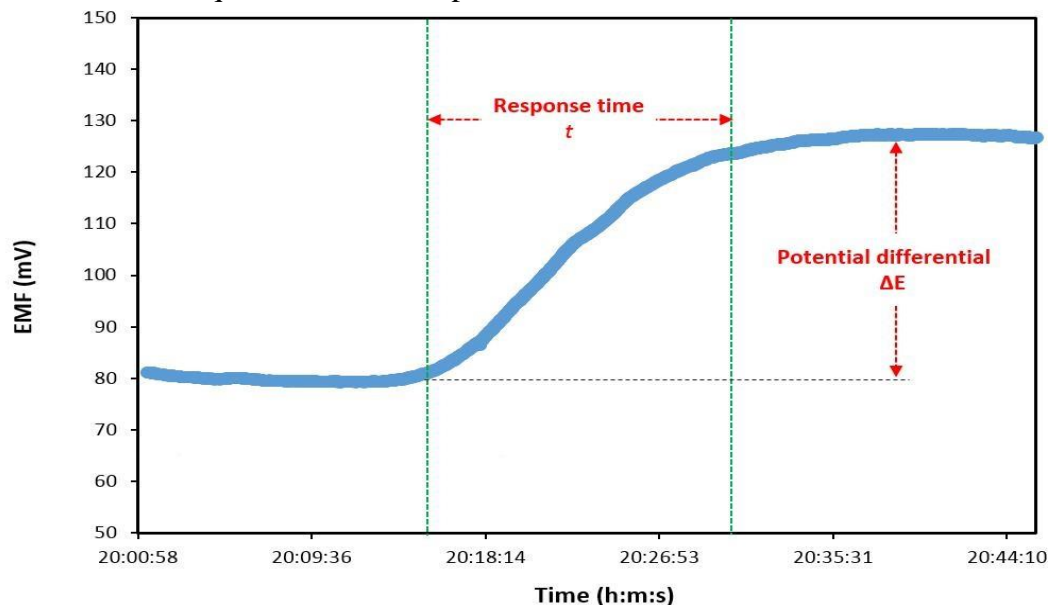


Fig. 5 A typical potential response of the CO<sub>2</sub> sensor.

Generally, an excess of citric acid was present in the system solution, All the NaHCO<sub>3</sub> reacted with the acid and transferred to the CO<sub>2</sub> following equation [2]. Thus, a certain quantity of CO<sub>2</sub> can be generated and employed automatically.



Fig. 6 illustrates the potential responses of the CO<sub>2</sub> sensor under pressure of 3000 psi. As shown in Fig.6, the base potential stabilized at 99 mV in 4101s. Then, NaHCO<sub>3</sub> was rapidly injected to the solution. The sensor output potential immediately increased and leveled off at 120 mV. The response time was 3461s as the CO<sub>2</sub> concentration was 0.001M. With the increase CO<sub>2</sub> concentration to 0.002 M, a similar behavior was observed, as depicted in Fig. 6. It can be found that the potential change is proportional to the CO<sub>2</sub> concentration directly. The potential change increased as the CO<sub>2</sub> concentration increased. The response time of the CO<sub>2</sub> sensor was found to be relied on the CO<sub>2</sub> concentration. Also the response time for the CO<sub>2</sub> sensor is on the order of 10<sup>3</sup> seconds at the operation pressure of 3000psi.

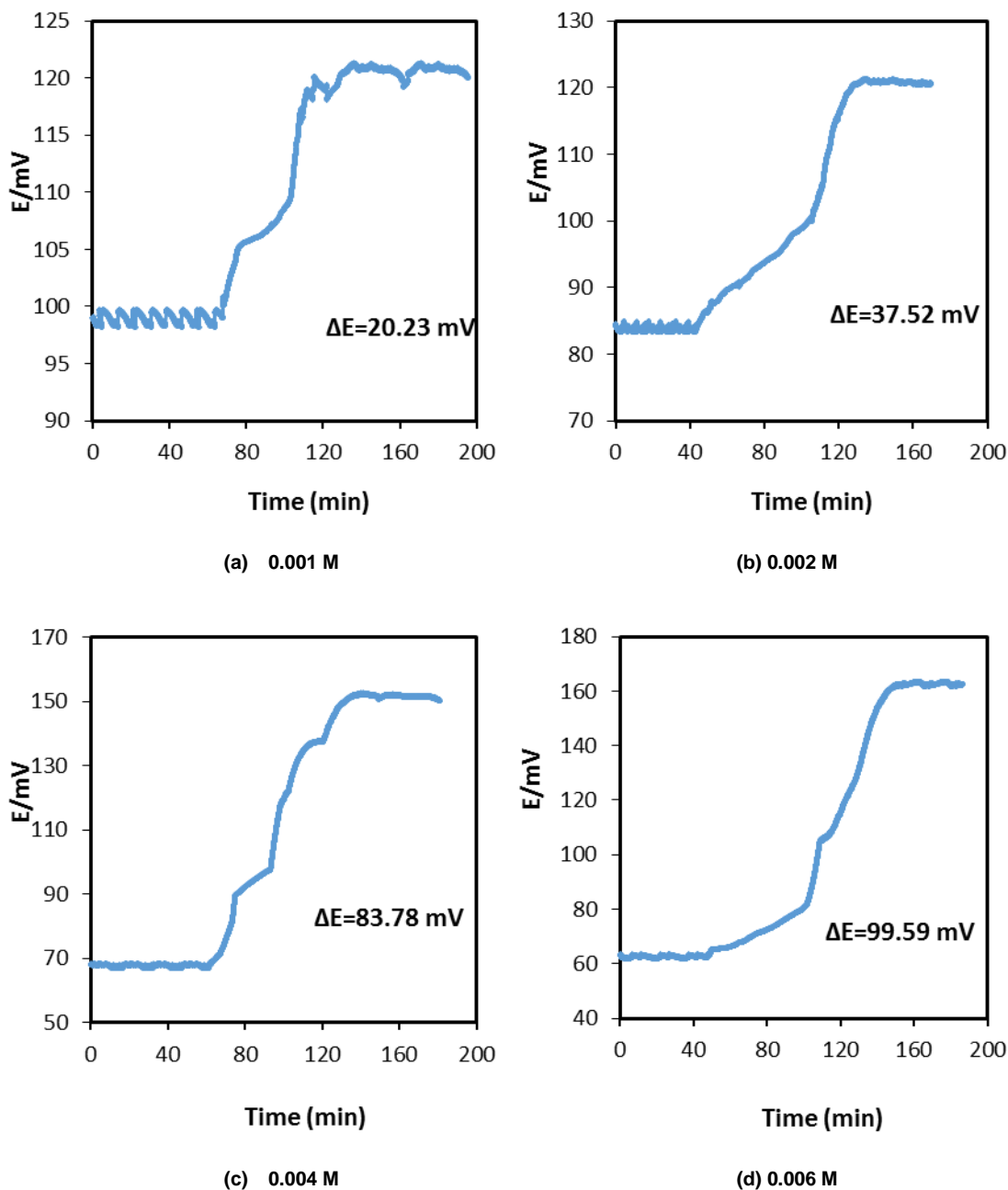


Fig. 6 Potential response of CO<sub>2</sub> sensor with the addition of NaHCO<sub>3</sub> in the 0.2 M citric acid-HCl solution at 3,000 psi, [NaHCO<sub>3</sub>] is (a) 0.001M, (b) 0.002 M, (c) 0.004 M and (d) 0.006 M.

### Monitor CO<sub>2</sub> migration in simulated CO<sub>2</sub> storage process

Fig. 7 presented the potential response of the CO<sub>2</sub> sensor for the coreflooding process. The results demonstrate that, when 2.0% brine was injected into the core, the output signal of the sensor was around 43.6 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 CO<sub>2</sub> began injection into the core, the output potential was the same as that in the brine flooding test for almost 3000s and then it suddenly increased to 243.1 mV. Apparently, as CO<sub>2</sub> injection was initiated, CO<sub>2</sub> moved forward



along the core and took 30 min to reach the sensor. The output potential of the sensor stayed unchanged before the CO<sub>2</sub> plume arrived. When the injected CO<sub>2</sub> reached the sensor, the CO<sub>2</sub> molecule diffused into the sensor and changed the pH of the internal solution, resulting in an immediate potential increase to 243.1 mV. The response time of the sensor, due to the high pressure and concentration of the CO<sub>2</sub>, was around 20 min. 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. 7, is 199.5 mV.

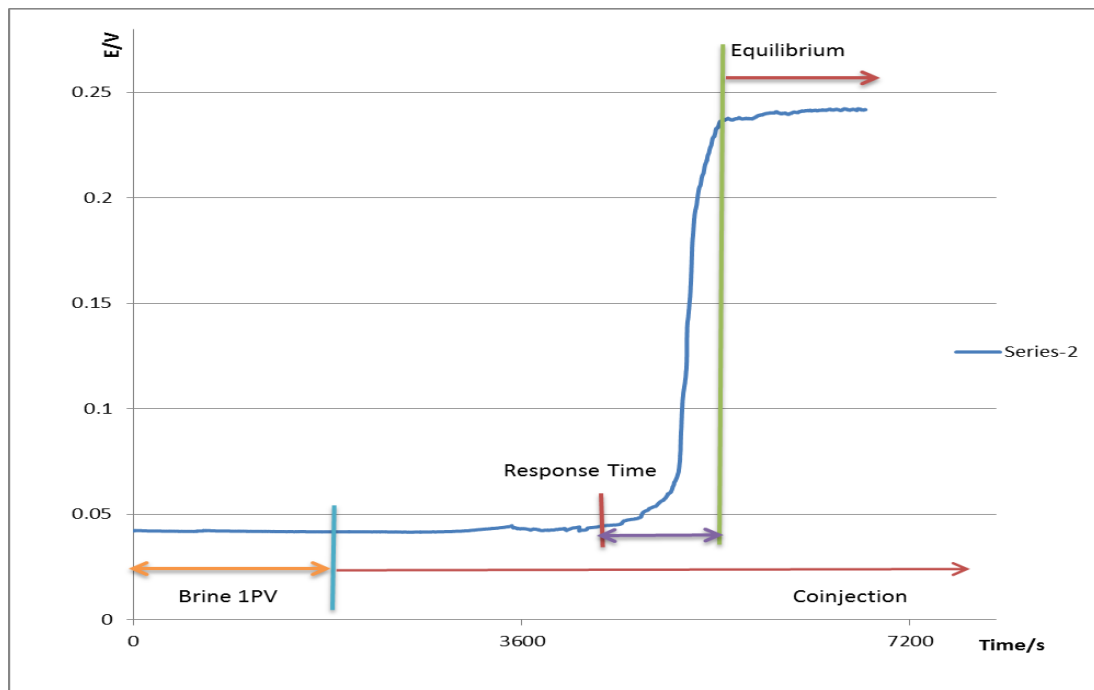


Fig. 7 Potential response of CO<sub>2</sub> sensor vs. Time—Series 2. Brine injection rate: 100mL/h; Co-injection rate: 100 mL/h

A second CO<sub>2</sub>/brine core flooding test was performed with the CO<sub>2</sub> sensor. This procedure was similar to the first test, except that the sensor was flooded with brine after the CO<sub>2</sub>/brine core flooding. Fig. 8 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 CO<sub>2</sub>/brine was injected into the core, indicating some dissolved CO<sub>2</sub> diffused into the sensor. After that, as 1 PV of CO<sub>2</sub>/brine was injected into the core, an abrupt potential increase was observed. This high potential increase indicated the CO<sub>2</sub> plume reached the sensor, as shown in Fig. 8. Then after the sensor was equilibrated with the CO<sub>2</sub> 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 CO<sub>2</sub> sensor can be recovered by brine flooding in CO<sub>2</sub> storage process. This is promising for the sensor application in WAG CO<sub>2</sub> storage operation. However, further tests need to be conducted to understand the sensor performance and lifetime in WAG operation.

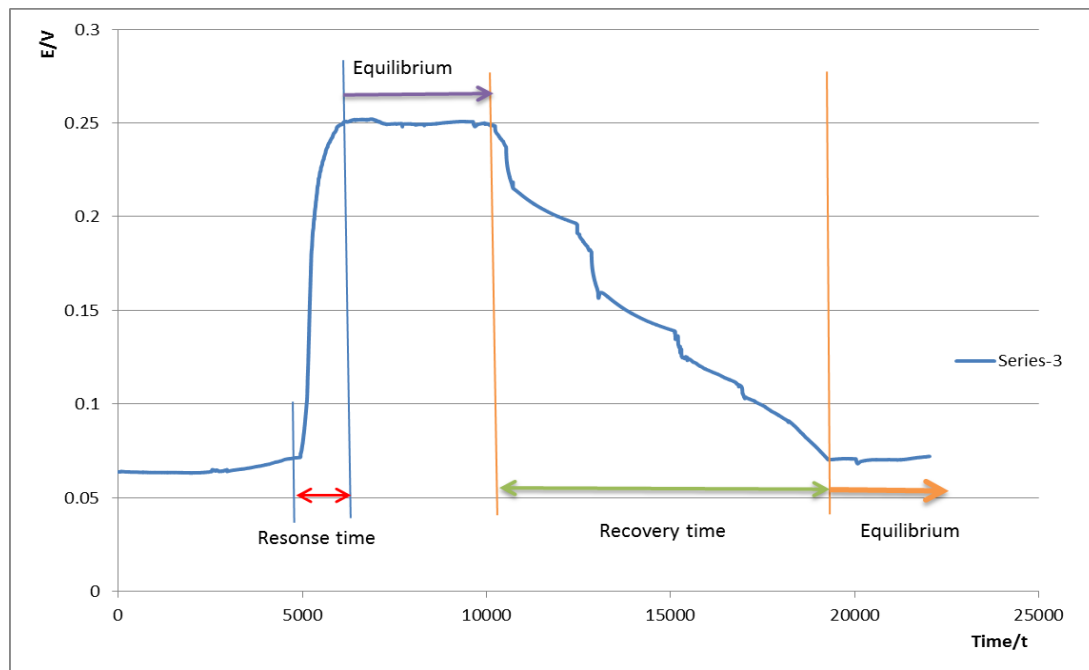


Fig. 8 Potential response of CO<sub>2</sub> sensor vs. Time---Series 3. Brine injection rate: 100mL/h; Co-injection rate: 100 mL/h; Secondary brine injection rate: 100mL/h

## Conclusion

An electrochemical downhole CO<sub>2</sub> sensor was developed and tested in the solution with different concentrations of CO<sub>2</sub> and displayed very good CO<sub>2</sub> sensing performance under high pressure. CO<sub>2</sub>/brine coreflooding tests were carried out to evaluate the performance of the CO<sub>2</sub> sensor in simulate CO<sub>2</sub> storage process. The results indicated that the sensor could detect CO<sub>2</sub> movement under the simulated reservoir conditions. Further studies showed that the sensor could be reused by brine flooding after CO<sub>2</sub>/brine flushed the core. The results of the core flooding tests demonstrated that the sensor had potential application for CO<sub>2</sub> monitoring in carbon storage.

## Acknowledgement

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