Study on Aqueous CO$_2$ Detection to Monitor the Potential Leakage of CO$_2$ Stored in the Ocean

SATO Hiroshi : Ph. D., P. E. Jp (Applied Science), Advanced Applied Science Department, Research Laboratory, Corporate Research & Development

AKIKUBO Kazuma : Advanced Applied Science Department, Research Laboratory, Corporate Research & Development

Carbon dioxide Capture and Storage (CCS) technologies have received considerable attention because of their potential application in preventing global warming by reducing the amount of greenhouse gases, in which carbon dioxide (CO$_2$) is regarded to be the main player. The storage of CCS must guarantee safety to the environment. In light of this, the technique for detecting CO$_2$, which exists in underwater environments, is one of the key component technologies for the practical application of carbon storage. In order to continuously monitor underwater CO$_2$ in ocean storage areas, indirect detection techniques — such as pH measurement — have been proposed. For practical application, however, a direct detection technique is required to ensure a more precise and sensitive method of monitoring underwater CO$_2$. In this study, electrochemical detection of CO$_2$ in a saline solution was performed using an amino group immobilized Au electrode. The oxidation and reduction currents related to the redox active compounds varied depending on the CO$_2$ concentration, suggesting that it is possible to directly detect aqueous CO$_2$.

1. Introduction

To restrain the increase in the concentration of CO$_2$ in the air, which is considered to be a cause of global warming, a technology called Carbon dioxide Capture and Storage (CCS) is being developed for practical application.[1], [2] As shown in **Fig. 1**, CCS consists of four processes; ① capture, ② transport, ③ injection, and ④ storage.[3] Among them, the storage process requires the longest period and involves long-term maintenance including leakage monitoring for safety assurance. Storage methods called geological storage and ocean storage are under verification and study. The former injects CO$_2$ into aquifers, and the latter keeps CO$_2$ in deep waters under high pressure.

Techniques have been proposed for monitoring leakage of CO$_2$ in geological storage and in ocean storage at the bottom of the sea. They are based on indirect measurements of CO$_2$, using changes in ionic species or changes in pH[4] in seawater as indicators. If a technology for directly measuring the CO$_2$ concentration in seawater is realized, it will be possible to detect CO$_2$ with higher sensitivity and thereby improve the leakage monitoring accuracy.

Chemical sensors detect particular substances at high sensitivity by using functional organic molecules that react with the substances (molecular recognition). Such sensors are applied in medical care, food, environmental monitoring and many other fields. As shown in **Fig. 2**, the detecting part of a chemical sensor consists of a "molecular recognition part" where functional organic molecules recognize the substance to be measured, and a "signal conversion part" where a signal is converted.

The signal conversion part is based on techniques such as ① electrochemistry, ② quartz oscillators, and ③ surface-plasmon resonance. Chemical sensors using electrochemical techniques are commonly used because it is easy to immobilize
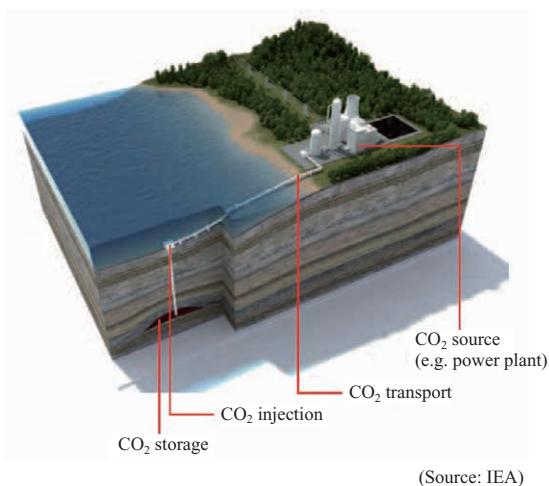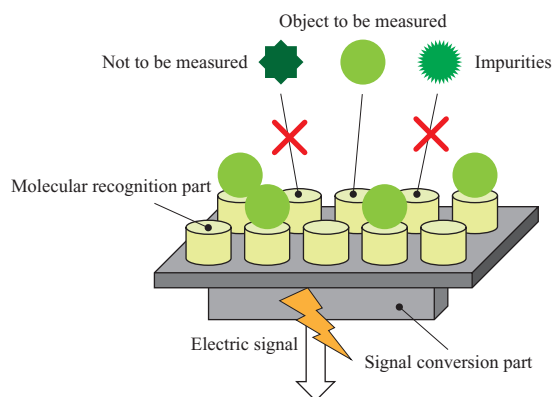

Fig. 1 Schematic illustration of a CCS system[3]

(Source: IEA)

Fig. 2 Configuration of a typical chemical sensor

functional organic molecules on electrode surfaces.[5]

In this study, an amine-modified electrode was investigated to prove the principle of a chemical sensor having the electrode surface modified with amines that bind selectively to CO_2 and thereby becoming capable of detecting CO_2 in water, and then an X-ray Photoelectric Spectroscopic (XPS) analysis was performed on the amines on the electrode surface. Another experiment was conducted to measure the CO_2 concentration by using a chemical sensor prepared by modifying the electrode surface with both amines and ferrocene, which is a redox active compound.

2. Experimental method

An experiment to prove the principle of the chemical sensor was conducted by preparing an amine-modified electrode with aminoethanethiol, which has a thiol group at the end of the molecular chain, and by preparing a measurement solution with potassium ferricyanide added as a redox active compound. After that, a chemical sensor electrode was prepared by modifying the surface with both aminoethanethiol and 6-(ferrocenyl) hexanethiol, which is a thiol derivative of ferrocene.

It is possible to form a Self-Assembled Monolayer (SAM) of molecules with thiol groups by preparing a dilute solution and immersing a gold (Au) electrode in it.[6] SAMs are widely used in the fields of chemical sensors and bio-sensors as a simple technique for immobilizing molecules on electrode surfaces.[7], [8]

Electrodes were prepared according to the following procedure.

(1) Au electrodes (with a diameter of 3 mm) were polished by using alumina slurry (with particle diameters of 1 μm and 0.3 μm) for 10 minutes each.

(2) The Au electrodes were sonicated in ion-exchanged water for 10 minutes to remove alumina slurry from their surfaces.

(3) An amine-modified electrode and an amine/ferrocene-comodified electrode were prepared by immersing one electrode in a 5 mmol/l aminoethanethiol solution (with ethanol as a solvent) and the other in a mixture of 2-aminoethanethiol (2.5 mmol/l) and 6-(ferrocenyl) hexanethiol (2.5 mmol/l) (with ethanol as a solvent) until a self-assembled monolayer was formed on each surface.

(4) The electrode surfaces were washed with ethanol and ion-exchanged water, and then stored in ion-exchanged water until the measurement.

To make electrochemical measurements, a cyclic voltammetry experiment was conducted by using a conventional three-electrode system composed of a Working Electrode (WE), a Counter Electrode (CE) and a Reference Electrode (RE). (Cyclic voltammetry is a technique for measuring redox potential by cycling the potential of the working electrode in a certain range.) The amine-modified electrode or the amine/ferrocene-comodified electrode was used as the WE, a platinum (Pt) wire was used as the CE, and a silver/silver chloride (Ag/AgCl) electrode was used as the

RE. A measurement solution was prepared by freshly preparing a 500 mmol/l sodium chloride (NaCl) aqueous solution to have salinity equivalent to that in seawater and then adding sodium hydrogen carbonate (NaHCO$_3$) to adjust the CO_2 concentration. The CO_2 concentration in the measurement solution was theoretically determined from the dissociation equilibrium of sodium hydrogen carbonate in the aqueous solution, and calculated on the assumption that 0.28% of the added sodium hydrogen carbonate exists as CO_2 molecules in the aqueous solution. When the amine-modified electrode was used as the working electrode, 5 mmol/l $K_4Fe(II)(CN)_6$ was added as a redox active compound. **Figure 3** shows the measurement system using the amine-modified electrode.

3. Results and discussions

3.1 Detecting CO_2 by using the amine-modified electrode

A cyclic voltammetry experiment was conducted to determine the redox reaction of ferrocyanide ions $[Fe(II)(CN)_6]^{4-}$ in the measurement solution by using the amine-modified electrode prepared as described above. As shown in **Fig. 4**, typical
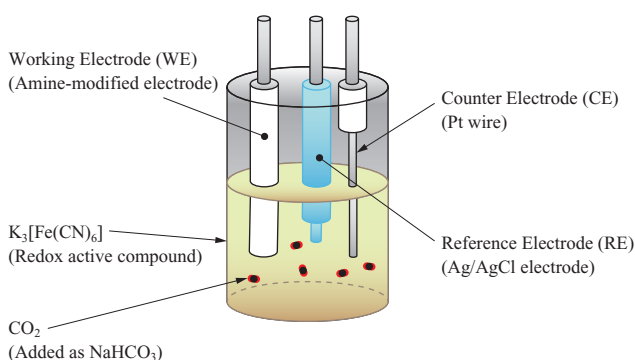

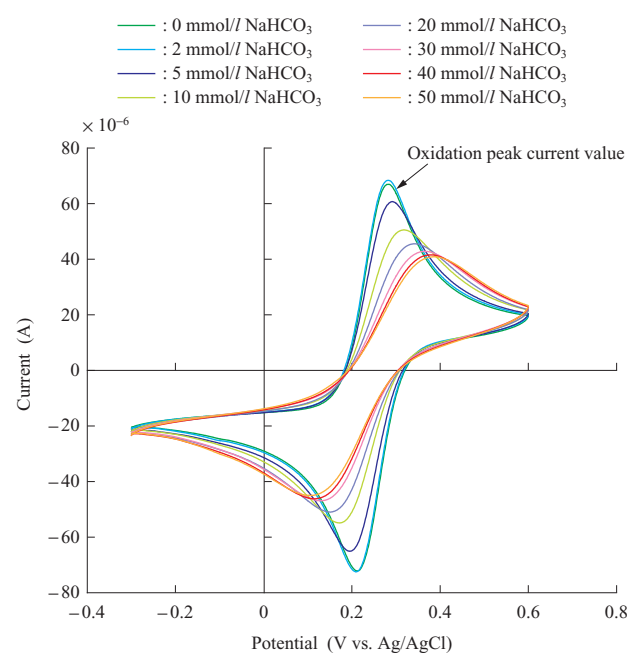Fig. 3　Measurement system for using the amine-modified electrode

Fig. 4　Cyclic voltammograms for the amine-modified electrode

cyclic voltammograms were obtained from the experiment, showing the response current derived from the redox of ferrocyanide ions $[Fe(II)(CN)_6]^{4-}$.

When the CO_2 concentration in the measurement solution was changed by adding sodium hydrogen carbonate, the response current value decreased with the increase in the concentration.

This is probably because negatively charged carbamate ions were generated on the electrode surface due to the increased CO_2 concentration and the resultant electrostatic repulsion impeded diffusion of probe molecules on the electrode surface.

As shown in **Fig. 5**, amines ($-NH_2$) on the electrode surface are neutral or positively charged in the absence of CO_2.

Thus, negatively charged ferrocyanide ions $[Fe(II)(CN)_6]^{4-}$ in the measurement solution easily reach the electrode surface where they can give and take electrons (**Fig. 5-(a)**). In contrast, in the presence of CO_2, amines on the electrode surface react with CO_2 and generate negatively charged carbamate ions. The resultant electrostatic repulsion prevents negatively charged ferrocyanide ions $[Fe(II)(CN)_6]^{4-}$ from reaching the electrode surface and giving or taking electrons (**Fig. 5-(b)**). Since the generation of carbamate ions is an equilibrium reaction, the amount of negative charge on the electrode surface varies depending on the CO_2 concentration in the measurement solution. This is considered to be the reason why the response current decreased depending on the concentration.

Figure 6 shows the XPS spectra of the Au-deposited substrate with the amine-modified surface. **Figures 6-(b)** and **-(c)** show the spectra for the substrate immersed in the measurement solution with different CO_2 concentrations, while **Fig. 6-(a)** shows the result in the absence of CO_2. The peak intensity derived from the N-H binding energy is higher in **Figs. 6-(b)** and **-(c)** than in **Fig. 6-(a)**. This is probably because amines on the electrode surface bound to CO_2 as shown in **Fig. 5**.

In this study, the electrode surface was modified with 2-aminoethanethiol, which is primary amines binding
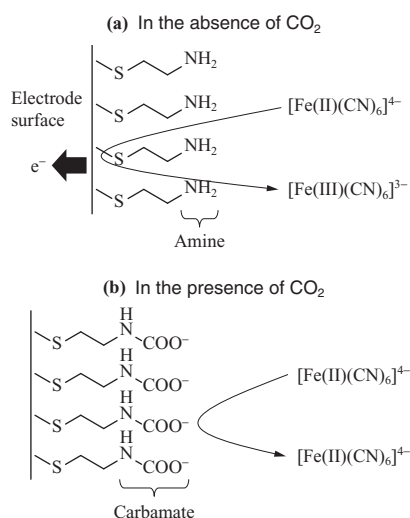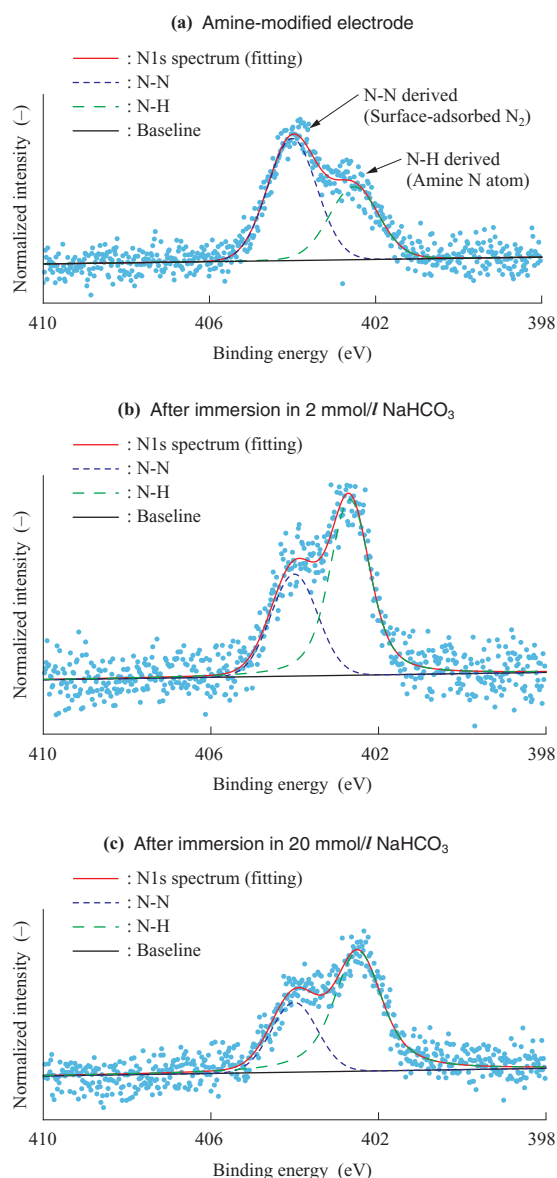

Fig. 6 N1s XPS spectra for the amine-modified Au substrate surfaces

strongly to CO_2, for the purpose of proving the principle. For all intents and purposes, this amine-modified electrode cannot be reused after detecting CO_2. We believe that it will be possible to achieve reversible detection applicable to practical use by modifying the electrode surface with amines that bind weakly to CO_2.

Next, analytical curves for CO_2 concentrations were drawn from the changes in the response current that were obtained from the experiment. **Figure 7** shows the analytical curves drawn based on the CO_2 concentration measurement using the amine-modified electrode.

The amino group modified electrode prepared in this study exhibited changes in the current depending on the CO_2 concentration ranging from 0.25 ppm (estimated from the carbonate concentration in seawater) to concentrations 10 times and 20 times higher than that. The CO_2 saturation concentration in water is approx. 1.5 ppm (25°C, 100 kPa). If
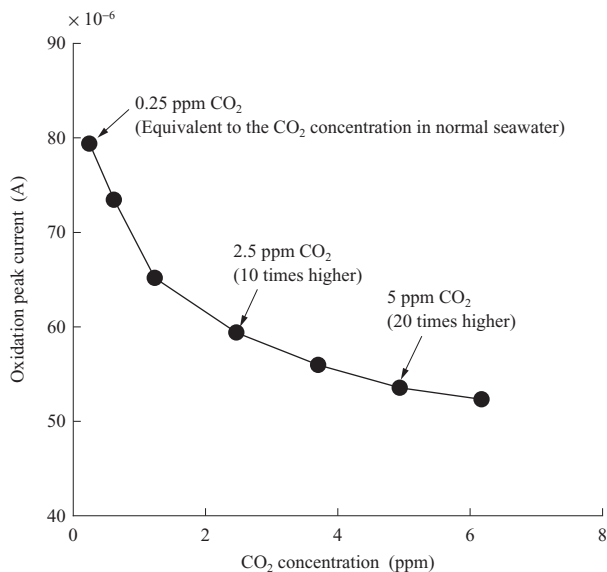

Fig. 5 Schematic illustrations of CO_2 detection using the amine-modified electrode

Fig. 7 Calibration curve for CO_2 concentration using the amine-modified electrode

the electrode can detect the CO_2 concentration that is adjusted by adding sodium hydrogen carbonate to 10 times higher than the CO_2 concentration in ordinary seawater, it can be used for leakage detection.

3.2 CO_2 detection by using the amine/ferrocene-comodified electrode

To measure the CO_2 concentration in seawater in a real situation, it is necessary to immobilize the redox active compound on the electrode surface along with the amines. **Figure 8** shows the results of an electrochemical measurement using an amine/ferrocene-comodified electrode, which was modified with both amines and ferrocene as redox active compounds. The response current derived from the redox of ferrocene immobilized on the electrode surface was obtained as the background current before sodium hydrogen carbonate was added. The ferrocene-derived response current (oxidation
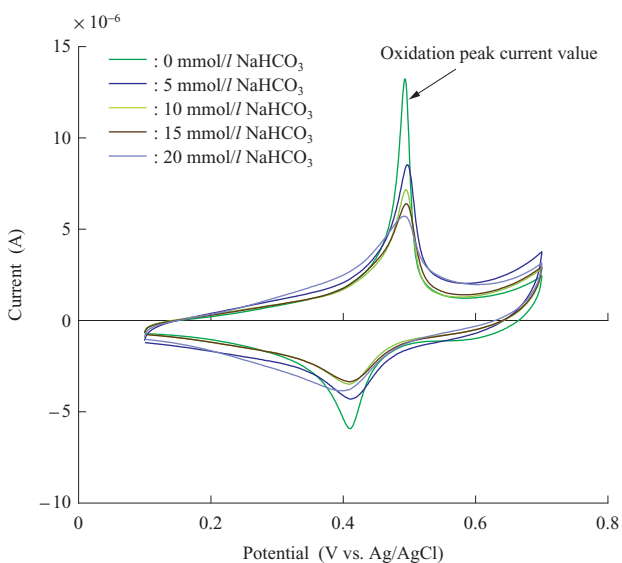
peak current value) decreased when the CO_2 concentration in the measurement solution was increased by adding sodium hydrogen carbonate.

This is probably because negatively charged carbamate ions were generated on the electrode surface due to the increased CO_2 concentration, as in the case of the amino group modified electrode, and the resultant electrostatic repulsion prevented the ferrocene oxidation reaction (transfer of electrons from ferrocene molecules to the electrode surface), as shown in **Fig. 9**.

Next, analytical curves for the CO_2 concentration were drawn from the changes in the response current that were obtained from the experiment. **Figure 10** shows the analytical curves drawn based on the CO_2 concentration measurement using the amine/ferrocene-comodified electrode. The amine/ferrocene-comodified electrode prepared in this study exhibited changes in the current depending on the CO_2 concentration ranging from 0.25 ppm (estimated from the carbonate concentration in seawater) to a concentration 10 times higher than that.
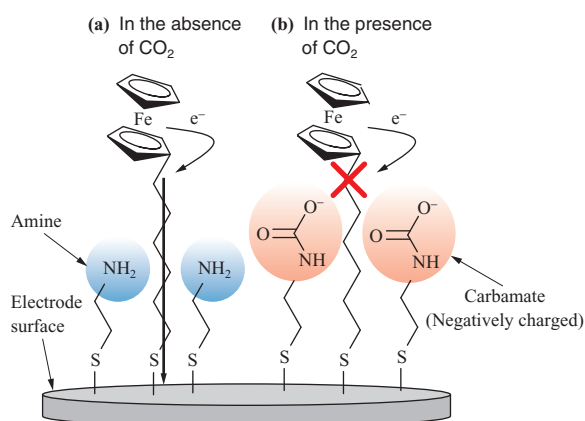

Fig. 9 Schematic illustration of CO_2 detection using the amine/ferrocene-comodified electrode

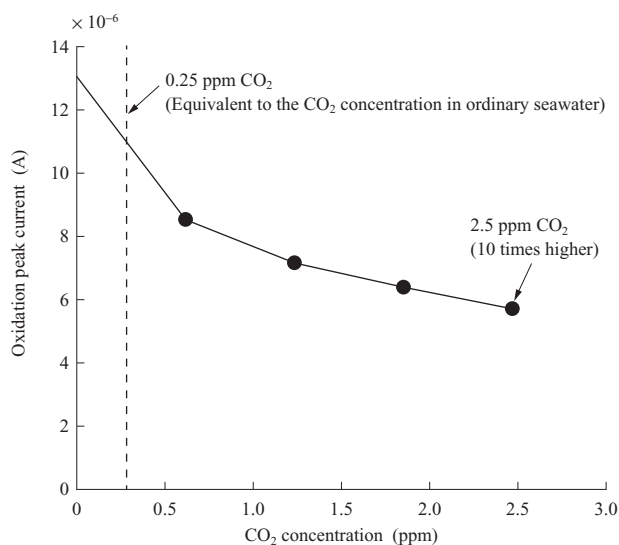**Fig. 8** Cyclic voltammograms for the amine/ferrocene-comodified electrode

Fig. 10 Calibration curve for CO_2 concentration using the amine/ferrocene-comodified electrode

4. Conclusion

In this study, an amine/ferrocene co-immobilized electrode was prepared by modifying the electrode surface both with amines, which bind to CO_2 and generate negatively charged carbamate ions, and ferrocene, which is a redox active compound, by immobilizing such substances on the electrode surface, and then the analytical curves for CO_2 concentrations were drawn accordingly. The response current decreased with the increase in the CO_2 concentration in the measurement solution, showing the responsiveness to the CO_2 concentration. This proved that the electrode can detect changes in the CO_2 concentration.

The sensor electrode prepared in this study exhibited changes in the current depending on the CO_2 concentration ranging from 0.25 ppm (estimated from the carbonate concentration in seawater) to a concentration 10 times higher than that. In the future, we will conduct tests by using actual seawater in consideration of the impacts of interfering substances other than sodium chloride, such as salt and organic matter, with a view to application to actual geological storage and ocean storage sites.

REFERENCES

(1) G. T. Rochelle : Amine Scrubbing for CO_2 Capture Science Vol. 325 No. 5 948 (2009. 9) pp. 1 652-1 654

(2) K. Takano : Toward the Realization of Low Carbon Coal-Fired Power Plant Journal of IHI Technologies Vol. 55 No. 4 (2015. 12) pp. 32-35

(3) OECD/IEA : Technology Roadmap : Carbon Capture and Storage 2009 (2009. 11) pp. 8-9

(4) K. Shitashima, Y. Maeda and A. Sakamoto : Detection and Monitoring of Leaked CO_2 through Sediment, Water Column and Atmosphere in a Sub-Seabed CCS Experiment International Journal of Greenhouse Gas Control Vol. 38 (2015. 7) pp. 135-142

(5) M. Tsuda : New Biophysics 6 Biological Super Sensor Kyoritsu Shuppan Co., Ltd. (1997. 7)

(6) R. Colorado Jr. and T. R. Lee : Thiol - based Self - assembled Monolayers - Formation and Organization Encyclopedia of Materials : Science and Technology (2001. 9) pp. 9 332-9 344

(7) S. Takahashi and J. Anzai : Phenylboronic Acid Monolayer-Modified Electrodes Sensitive to Sugars Langmuir Vol. 21 (2005. 4) pp. 5 102-5 107

(8) H. Sato and J. Anzai : Preparation of Layer-by-Layer Thin Films Composed of DNA and Ferrocene-Bearing Poly(amine)s and Their Redox Properties Biomacromolecules Vol. 7 (2006. 5) pp. 2 072-2 076