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The use of an amine-functionalized electrode for the electrochemical detection of carbon dioxide in the ocean

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Abstract

This research will report on the electrochemical detection of CO2 in a salt solution and the development of a sensor electrode modified with an amino group. The carbon dioxide concentration in an aqueous solution of redox-active potassium ferricyanide was measured electrochemically using the cyclic voltammetry method. The quantity of carbon dioxide molecules in the measuring fluids has altered the oxidation/reduction process peak currents in cyclic voltammograms. The CO2 concentration calibration curve was generated by tracing the peak currents during oxidation. The CO2 content in typical seawater may be estimated to be up to 20 times higher than using the sensor electrode produced in this work.

Introduction

This study details the creation of an amino-modified sensor electrode for electrochemical CO2 detection in a salt solution. Electrochemical cyclic voltammetry was used to determine the concentration of carbon dioxide in an aqueous solution containing redox-active potassium ferricyanide. Peak currents in cyclic voltammograms representing the oxidation/reduction process have been shifted due to the presence of carbon dioxide molecules in the measurement fluids. Calibration curve for CO2 concentration was derived by following the peaks in oxidation currents. Using the sensor electrode developed in this study, the CO2 level of normal seawater might be predicted to be up to 20 times higher. a great degree of selection and sensitivity Chemical sensors have a detector and a transducer. Functional organic groups on the molecules being examined are recognized by detector components. However, transducer components transform molecular recognitions into signals such as electrochemical signals, surface plasmon resonance, change in mass, etc. Electrochemical measurement is extensively employed for the transducer component since surface modification methods for the electrode surface are so prevalent. Inorganic compounds containing amino groups are known to react with carbon dioxide to produce carbamate ions. Solvents for the CCS capture process have been the subject of research as recently as [2–4], with a focus on a variety of alkanolamines and their blends. Using amino groups as the sensor component, it is expected to be possible to create a chemical sensor capable of direct measurement of CO2 molecules. This study will present the electrochemical detection of CO2 in a salt solution using an electrode functionalized with amine. Couplings of CO2 molecules to the immobilized amino groups on the electrode were evaluated by measuring the electrochemical responses. Electrochemical responses for CO2 concentration are plotted to generate the calibration curve.

Materials and Methods

Kanto Kagaku Co. (Tokyo, Japan) and Tokyo Kasei Co. (Tokyo, Japan) supplied the aminoethantiol and potassium hexacyanoferrate (III), respectively. Both the sodium chloride and the sodium bicarbonate came from

Showa kagaku Co. (Tokyo, Japan). Everything was utilized just as it had been delivered, and it was everything of the best quality possible.

Preparation of Amine-modified Electrodes

A gold (Au) disk electrode (diameter, 3.0 mm) was used. First, the surface of the electrode was polished thoroughly with aqueous slurries of alumina paste and then rinsed with water, gently. The Au electrode was dipped in a freshly prepared aminothiol aqueous solution (10 mM) overnight to fabricate self-assembled monolayer (SAM) which has amino groups in the end of molecular chain, and then the electrode was rinsed with water, gently.

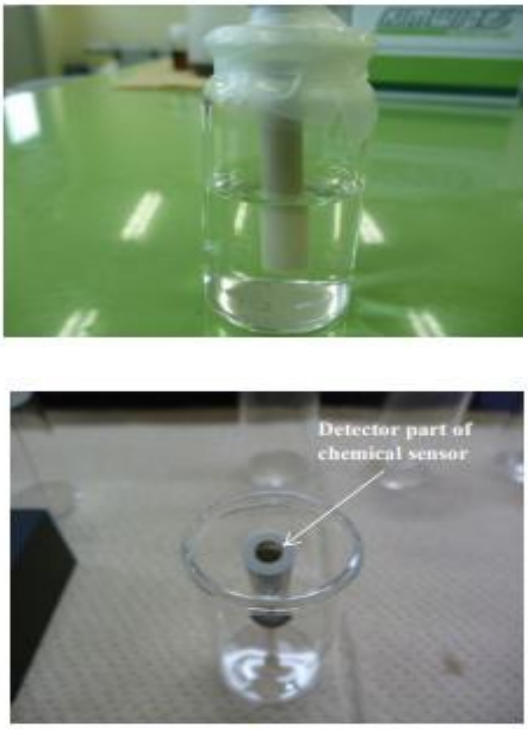
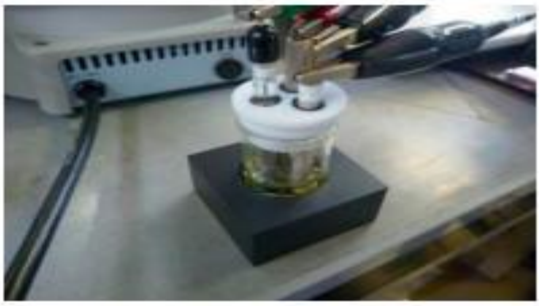


Fig. 1. Fabrication of amino group terminated SAM on the Au electrode; immersion set-up of the electrode (left) and surface of the electrode immersed overnight (right).



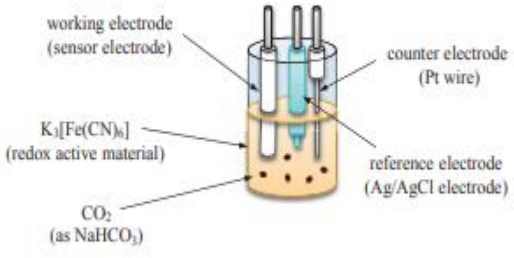


Fig. 2. Experimental set-up for electrochemical evaluations of the sensor electrode.

Electrochemical Evaluations

The amine-functionalized electrode's electrochemical properties were evaluated using a standard three-electrode setup, including a platinum wire counter electrode and an Ag/AgCl electrode reference electrode. Everything was measured when it was at room temperature.

$$NaHCO_3(s) \rightarrow Na^+ + HCO_3^- \quad (1)$$
$$HCO_3^- + H^+ \rightarrow H_2CO_3(aq) \quad (2)$$
$$H_2CO_3(aq) \rightarrow H_2O(aq) + CO_2(aq) \quad (3)$$

An aqueous solution of 500 mM sodium chloride was used to generate a measuring solution for electrochemical assessments comprising potassium hexacyanoferrate (III) (5 mM) and sodium bicarbonate (0 to 50 mM). The concentration of sodium bicarbonate, which, by chemical equilibrium in water, may give rise to CO2 molecules, was varied to control the solubility of CO2 in the solution.

Results and discussions

The carbon dioxide concentration in an aqueous solution of redox-active potassium ferricyanide was measured electrochemically using the cyclic voltammetry method. A cyclic voltammogram (CV) and resulting calibration curve are shown in Figure 3. Currents for the oxidation and reduction of ferricyanide anions are presented in the left side of Figure 3. In addition, the oxidation and reduction peak currents have altered in response to the concentration of sodium bicarbonate supplied; raising the concentration of CO2 molecules by adding sodium bicarbonate results in a decrease of both currents. In the right side of Figure 3, we see the CO2 concentration calibration curve derived by graphing the oxidation peak currents of CVs. The graph clearly demonstrates that the sensor electrode developed in this work can distinguish between the background concentration of CO2 in seawater (0.25 ppm) and concentrations 10 and 20 times higher. Figure 4 depicts the underlying processes that cause a shift in electrochemical reactions with respect to the CO2 content of the measurement solutions. Because the amino groups are neutral in equilibrium, ferricyanide anions may readily migrate to the electrode surface when CO2 molecules are absent (Figure 4, upper left). Negatively charged carbamate anions are formed when carbon dioxide molecules combine with amino groups on the electrode surface (right side of Figure 4). Then, it is hypothesized that oxidation and reduction current are attenuated due to the electrostatic repulsion between ferricyanide and carbamate anions.

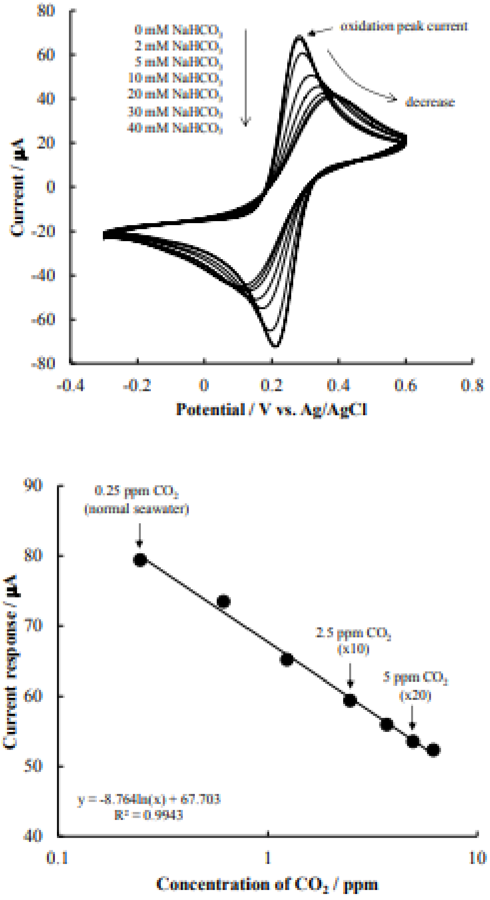


Fig. 3. Cyclic voltammograms of amino group-modified sensor electrodes at 100 mV s-1 of scan rate (left) and the calibration curve obtained by plotting electrochemical responses for CO2 concentration (right).

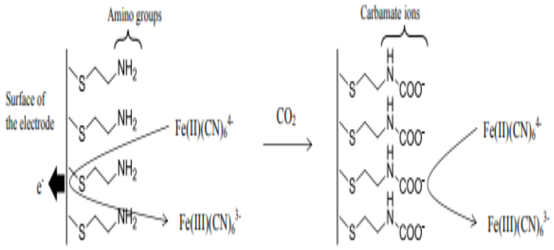


Fig. 4. Schematic illustrations of electrochemical reactions on the electrode surface at absence (left) and presence (right) of CO2 molecules in the solution.

Conclusions

The CO2 in the salt solution was detected electrochemically using an Au electrode modified with an amino group. The quantity of CO2 molecules in the measuring solutions affected the redox currents of the ferricyanide anions undergoing oxidation and reduction. Prepared sensor electrodes in this work can assess a 20-fold change in CO2 concentration compared to normal seawater.

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