The Winner's Article of the First Dr. Masao Horiba's Award

Development of an ISFET Sensor for In-situ pH Measurement in the Ocean

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The pH of seawater is an important factor that affects the thermodynamic state of all various acid-base systems and biological activity in the ocean. In recent years, in-situ measurement using pH sensors has attracted attention in relation to global warming issues. The pH sensor which uses an ion sensitive FET for the pH electrode, and a chlorine ion selective electrode for the reference electrode, can measure pH of seawater through the water column with high precision. Both these electrodes have solid-type construction and therefore have high pressure and shock resistance and can be used satisfactorily in deep sea conditions. In the field, the response speed of the developed pH sensor is 1 second or less, and the measurement accuracy is ±0.005 pH. This pH sensor can also be used with a $p\mathrm{CO_2}$ sensor by sealing the electrode with a gas permeability membrane.

Introduction

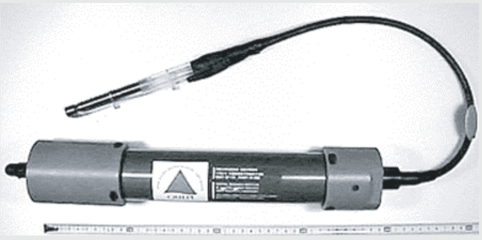
The pH of seawater is an important oceanographic factor reflecting processes such as the thermodynamic balance of chemical species dissolved in seawater and production/respiration associated with biological activity. The first measurement of pH of seawater was performed by Sorensen and Plalizsch in 1910. The pH measurement of seawater using glass pH electrodes has continued as a fundamental onboard analysis item of marine research since then. In recent years, in relation to global warming, the capacity of carbon dioxide absorption by the ocean came to attract attention as one of the most important research subjects. For this assumption it is necessary to have accurate knowledge of each concentration of the oceanic carbonate species (carbon dioxide, free carbonic acid, bicarbonate ions, carbonate ions). Only the partial pressure of carbon dioxide ($p\mathrm{CO_2}$) can be measured directly in these species. Since the equilibrium constant of the oceanic carbonate species is known, each concentration can be calculated if any two of the four parameters (alkalinity, total $\mathrm{CO_2}$, $p\mathrm{CO_2}$, and pH) are measured. Therefore, onboard analysis of these four parameters has been performed during many research expeditions[1].

However, there is a space/time limitation on the number of sampling stations and layers in conventional observations in that the main subjects are sampled and analyzed from water taken onboard, therefore it is difficult to perform wide-ranging measurements from large areas. From such a background, the development of chemical sensors or analysis devices for in-situ measurement and their application in the field was anticipated . The purpose is making consecutive vertical observations and prolonged consecutive observations in oceanic water columns.

Development of a pH Sensor for In-situ Measurement using ISFET

Approximately 40 years ago, in-situ pH measurement in the deep ocean began[2]. At that time, the method of alleviating the pressure differences within the equipment was by filling the space around the glass pH electrode with silicone oil. This is still the method presently used in glass pH electrodes marketed for deep-sea use by oceanographic instrument manufacturers. However, this type of glass pH electrode still has many problems such as slow response time, poor accuracy and resolution for correctly measuring the chemical processes of the ocean. In pH measurement using potentiometry, the ion sensitive FET (ISFET: Ion Sensitive Field Effect Transistor) which is a semiconductor, is used besides a glass pH electrode. The ISFET device was developed in order to measure the concentration of hydrogen-ions in aqueous media[3],[4] and was mainly aimed at medical applications[5]. It has high accuracy, quick response and good stability compared with other electrodes. Because there is no increase in electrode resistance and the stability remains high even if the sensor size is minimal, miniaturization is relatively easy. For these reasons, I started development of a pH sensor using an ISFET for the pH electrode to obtain in-situ high precision measurement of seawater pH from the surface to substantial depths. The ISFET, which is a semiconductor, is a solid-state electrode, so it can be used without special preparation for work under high pressures such as in the deep ocean. As a first step, a prototype in-situ pH sensor (Ver. 1) was built using a comparatively easy-to-design analog pH amplifier, and several sea trial tests were performed. After this, the next in-situ pH sensor was developed (Ver. 2) which was based on the results of the sea trial tests of the first version. This had a digital pH amplifier which was greatly miniaturized (Figure 1).

(a) In-situ pH sensor Ver. 2 (400(L) × 55(ϕ))



(b) Electronic circuit board (200(W) × 30(D))

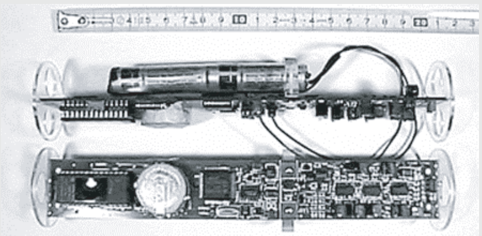


Figure 1 In-situ pH Sensor using ISFET (Ver. 2)

Figure 2 shows the pH sensor of Ver. 1 and Ver. 2. This used a pressure-compensation-type silver/silver chloride reference electrode[6]. This is usually used for pH measurement under high temperature high-pressure water environments as a reference electrode in specific applications, such as in nuclear power plants. The inner solution was saturated sodium chloride solution. As a result of sea trial tests of this pH sensor in the ocean, it has been confirmed that the ISFET electrode is very effective for in-situ pH measurement[7].

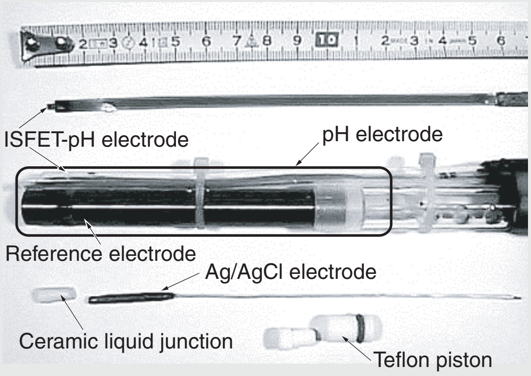


Figure 2 View of pH Electrode of In-situ pH Sensor Ver. 2

An Assessment of the Reference Electrode

The stability of the reference electrode is important for measuring pH. However, it is clear that there are problems with response time and accuracy when using the silver/silver chloride reference electrode (as used in the sensors of Ver. 1 and Ver. 2). There is also deterioration of the inner solution of the reference electrode, causing changes to the reference values when performing long-term pH measurement. It is clear then, that a reference electrode that can perform long-term pH measurement with a quick response and high accuracy is needed.

Seawater is an electrolyte solution that contains chlorine ions in high concentration. Except for coastal areas, salinity is almost constant in seawater. Therefore, a new type of electrode without an inner solution and liquid junction was examined utilizing seawater as the inner solution. At first, a platinum wire fused with silver chloride (the internal electrode of a pressure-compensation-type silver/silver chloride reference electrode) was tested as a reference electrode (Figure 3(a)). However, I confirmed that the electric potential fluctuates in seawater with the change in quality of the inner solution of the reference electrode and the formation of chemical compounds between silver and chemicals in seawater such as bromine. Next, an approximately 50 cm length of platinum wire on which silver chloride was electro-deposited, sealed with an ion exchange membrane tube of 45 cm length and formed into spiral shape. It was then filled with saturated sodium chloride solution and tested (Figure 3(b)). Although the drift of this reference electrode was small after several days, it turned out that this electrode finally forms chemical compounds with silver, just like the silver/silver chloride type reference electrode[8].

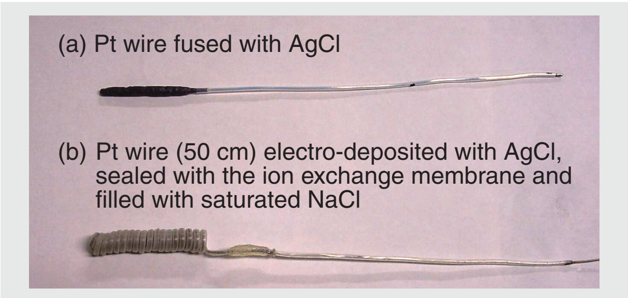


Figure 3 Silver/Silver Chloride Electrode Examined as Reference Electrode

Since the salinity of seawater is almost constant as mentioned above, the solid-state chlorine ion selective electrode (Cl-ISE) which responds to chlorine ions (the major element in seawater) was examined as a reference electrode for the in-situ pH sensor. The Cl-ISE is a pellet made of several chlorides. It is expected that the Cl-ISE will show a quick response time and long-term stability of electric potential in seawater because it has no inner solution. Looking at the results of a comparison between Cl-ISE and the silver/silver chloride reference electrode, Cl-ISE showed a very quick response, high stability, and the potential was stable in a wide salinity range.

On the other hand, I confirmed that the electric potential of Cl-ISE as the reference electrode changes at low salinity range (lower than 5‰). Therefore, caution is required when the reference electrode of Cl-ISE is used at low salinity locations such as estuaries or brackish water regions[8].

Improvement and Application of the In-situ pH Sensor

The electronic circuit board of the pH conversion amplifier and the data logger were newly designed for the Cl-ISE reference electrode. The heart of the pH converter used a high-resolution amplifier and the pH conversion amplifier and the data logger could be separated. Two kinds of pH conversion amplifier were made, one for the ISFET and one for potentiometry, so that different pH electrodes could be used (Figure 4). Figure 5 shows the newly developed in-situ pH sensor (Ver. 3). The calibration of the pH sensor was performed before and after in-situ measurement using two SWS scale standard solutions (seawater base standard solution for pH measurement of seawater[9]). In the field, the response time of the pH sensor is 1 second or less, and the accuracy is ±0.005 pH. After performing in-situ measurement in various locations of the ocean using the newly developed sensor, high accuracy, quick response, and long-term stability have been achieved[8].

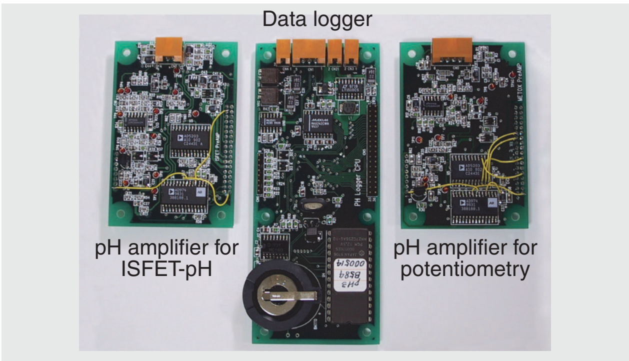


Figure 4 Two Types of pH Amplifier and Data Logger

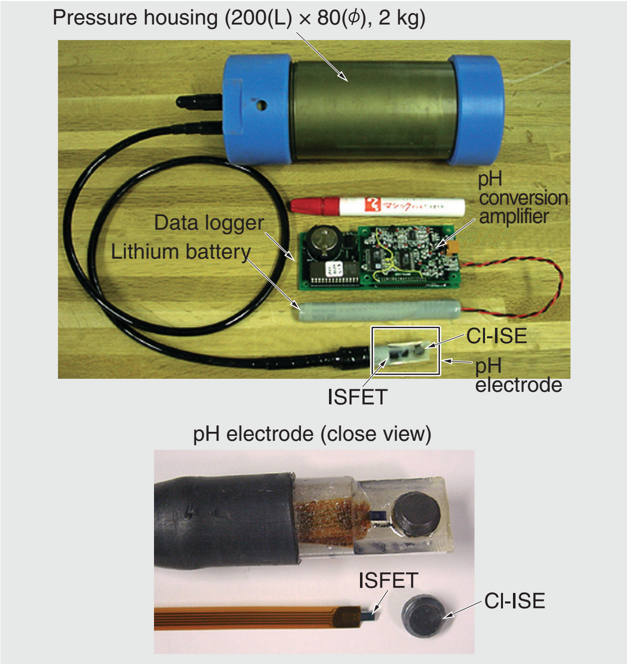


Figure 5 Newly Developed In-situ pH Sensor (Ver. 3) and pH Electrode

The newly developed pH sensor was then applied to development of the pCO_2 sensor for in-situ pCO_2 measurement in seawater, and sea trial tests were performed. The principle of pCO_2 measurement is as follows: the pH electrode and the Cl-ISE (chlorine ion selective electrode) of the pH sensor are sealed with a gas permeable membrane filled with the inner solution. The pH sensor can detect the pCO_2 change as the inner solution pH changes which is caused by penetration of carbon dioxide through the membrane. An amorphous Teflon membrane manufactured by U.S. DuPont (Teflon AF™) was used as the gas permeable membrane for this pCO_2 sensor. The sea trial tests showed that stable pCO_2 measurement was possible[10].

Additionally, a pH sensor that uses an indium oxide pH electrode, was examined by using the potentiometry pH conversion amplifier. Although the response time of indium oxide pH electrode was a little inferior to that of ISFET, I confirmed that an indium oxide pH sensor can be used as an in-situ pH sensor. Since a pH sensor which combines an indium oxide electrode and Cl-ISE is the perfect solid-state pH sensor, it can be used for in-situ pH measurement in extreme environments such as in sediment or drilling bore holes on the seabed or on land.

Oceanography-application of the pH Sensor

As for the next generation of chemical oceanography, possible research applications for in-situ pH sensors are as follows:

1. Collecting of pH and pCO_2 data in wide areas of ocean, horizontally and vertically, to study the processes controlling the oceanic carbon cycle and its interaction with the atmosphere.
2. In-situ measurement of the dissolution rate of calcium carbonate in pore water and the monitoring of biological activity in sediment.
3. Mapping and long-term monitoring of hydrothermal plumes to aid the understanding of the process of hydrothermal discharge to the ocean.
4. Real-time and/or long-term monitoring of the Earth interior using the bore holes left after ocean drilling.
5. Assessment (monitoring a pH decrease area and predicting the recovery period from low pH back to normal seawater pH conditions) of the environmental impact of the carbon dioxide ocean sequestration to mitigate global warming.

There are great expectations from research into the oceanic carbon cycle. As mentioned above, if the pH and pCO_2 of seawater can be measured simultaneously, all the equilibriums of carbonic acid substances in seawater can be calculated. In the medical field, a pH/pCO_2 sensor has already been developed. The long-term observations obtained from application of the pH/pCO_2 sensor will contribute to the understanding of the oceanic carbon cycle and the changes taking place in the Earth environment. For that purpose, it is necessary to have self-calibrating functions and to ensure high measurement accuracy in the field. Furthermore, in the oceanic carbon cycle, the estimate of the dissolution speed of the calcium carbonate in pore water and settling particles is also important. Although pH increases by dissolution of calcium carbonate in the ocean, because the pH change rate is very small, a highly sensitive and precise pH sensor is required. Since biological activity plays the important role of fixation of carbon dioxide levels in the ocean, long-term monitoring of pH changes by using highly sensitive pH sensors is foreseen.

In the deep-sea hydrothermal system, various chemical substances of magma enter the ocean through seawater-rock reactions under high temperatures and pressures. In-situ pH measurement in the deep-sea hydrothermal system is important for understanding metallogenetic process and the oceanic geochemical cycle[11],[12]. The International Ocean Drilling Program (ODP) and the Ocean Drilling the 21st century (OD21) plan to apply the chemical sensors to the long-term in-situ monitoring of chemical flux by utilizing bore holes after drilling. The understanding of the structure of the Earth's interior and the real time monitoring of the diastrophism that causes earthquakes will become possible through use of pH sensors. The pH sensor will be useful for "medical treatment of Earth itself".

In carbon dioxide ocean sequestration, the pH of seawater containing very high concentrations of liquid carbon dioxide is decreased (max. approximately pH 3), because carbon dioxide is acidic. It is very important to assess the effect of the ocean environment including ocean organisms to this pH depression caused by carbon dioxide ocean sequestration. For this reason, it is necessary to examine the environmental impact assessment methods about the influence of this carbon dioxide affecting the ecosystem of the ocean. Furthermore, the predictions of the diffusion range of low pH seawater (environmental impact range) and the recovery period from a low pH to a normal pH condition (environmental restoration time) are important items for assessing the environmental impact of carbon dioxide ocean sequestration. If many pH sensors for in-situ measurement are deployed (moored) around a carbon dioxide sequestrated region, they will be very effective as a tool for the prediction of environmental impact range and environmental restoration time[13].

Conclusion

In conclusion, because the needs of pH sensor are high in the field of medical treatment, clinical medicine and biomedicine, in-situ measurement using pH sensors is progressing well. Unfortunately application of in-situ sensors has not progressed so much in other fields. In order to develop a pH sensor for ocean use, it is necessary for the cooperation of specialists in not only oceanography but also in analytical chemistry, synthetic organic chemistry, polymer chemistry, electrochemistry, electricity and mechanical engineering.

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