

pH measurement in the ocean

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For a century since Cremer (1906) discovered glass membrane potential and Sørensen and Palitzsch (1910) measured ocean pH for the first time, glass electrodes have been used universally to measure ocean pH.

The ion sensitive membrane of the indicator electrode is a thin fragile glass film. The principle behind the selective response of the glass membrane electrode to hydrogen ions is unknown, and manufacturing process is a black boxes varying among manufacturers. Since Ag-AgCl electrodes are used for both the indicator and reference electrodes, they react with the sample solution and deteriorate. In addition, the reference electrode is constantly leaking internal solution to maintain conductivity with the indicator electrode through the sample as a salt bridge, and the solution needs to be replaced. Despite the vast amount of pH data accumulated by glass electrodes, the values are considered less reliable than those obtained by spectrophotometry due to drift and degradation of the electrodes without proper calibration (Dickson 1993, McLaughlin et al. 2017). The measurement of ocean pH by spectrophotometry was established by Clayton and Byrne (1993). Seidel et al. (2008) evaluated a in-situ measurement system as a precision of 0.0007 and accuracy of 0.0017. However, spectrophotometric measurement requires mixing of reagents for coloring the sample, which poses a limitation of in-situ measurement.

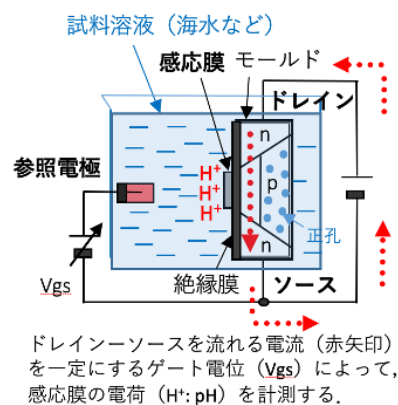
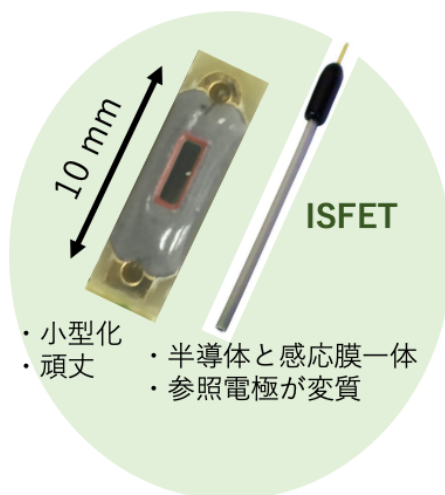
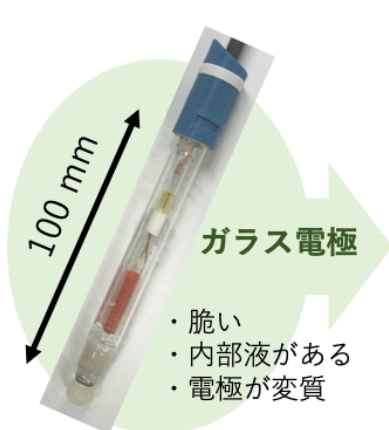
Since 1970, a pH sensor using a solid-state semiconductor was developed and put into practical use (Bergveld 1970). This is called an ISFET (Ion Sensitive Field Effect Transistor), which measure the potential of the ion-selective membrane (e.g. Ta_2O_5) by the transistor. The principle of ISFET is electrochemically clear and there is no black box. The semiconductor sensor is durable and can be reduced its size. ISFETs are also applied in Argo Float for pH measurement. The most commonly used Durafet sensor has a short time accuracy (repeatability) of 0.0005, a multi-year accuracy of 0.005, and an accuracy of 0.01 (Martz et al. 2010, Johnson et al. 2016).

However, since the semiconductor should be immersed in the solution united with the membrane, the semiconductor must be tightly molded. For deep-sea measurements, a pressure resistance of 10 MPa or higher is required. Pressure dependancy of the semiconductor must be taken into consideration for measurement in deep sea. Also, there is a limit for reduction in size of the semiconductor. In addition, Ag-AgCl is used as the reference electrode, which reacts with the chloride ions in the solution, causing the electrode to deteriorate. KCl gel is used as the internal solution of the reference electrode, and its replacement is also necessary.

The pH is the most fundamental chemical variable in the ocean. In particular, ocean acidification due to rising atmospheric CO_2 has been recognized as a new issue related to global environmental change, and pH measurement has become increasingly important. In addition to pH, the three other variables of the four measurable ones of the ocean carbonate system (pH, CO_2 , total inorganic carbon, and alkalinity) can be determined by adding acid to the seawater sample (total inorganic carbon and alkalinity) or by extracting CO_2 through a gas permeable membrane into the solution (CO_2 , total carbon dioxide) and measuring its pH. The development of a pH sensor that can maintain stability and accuracy even in seawater and high-pressure deep waters will greatly advance the monitoring of the ocean's carbonate system, based on which ocean acidification and the ocean's CO_2 sink capacity would be evaluated. The new pH sensor must be small, have low power consumption, be reagent-free, be stable over the long term, not be altered by seawater, be resistant to high pressure, and have little been dependent on pressure. The

precision and accuracy must be within 0.0002 and 0.001 considering the propagation of errors in calculating the carbonate system.

Keywords: pH, ocean, measurement, Ocean Acidification, ISFET



ISFET の原理