LONG-TERM GOALS

The long-term goals of this project are to enable observations of pH in the ocean using sensors deployed on autonomous platforms. These systems will enable robust, basin-scale observations of changing pH driven by natural and anthropogenic processes.

OBJECTIVES

Develop a robust and stable pH sensor for deep-sea applications that is based on the Honeywell Durafet Ion Sensitive Field Effect Transistor (ISFET). The sensor should operate to depths of at least 2000 m. It should have a precision of ±0.001 pH and a stability of 0.005 pH over periods up to 5 years throughout the oceanic temperature and salinity range.
APPROACH

Our laboratory experiments (Martz et al., 2010) have shown that the Honeywell Durafet pH sensor has the stability, precision and speed needed for long-term, in situ pH measurements. However, the commercially available version of the Durafet is only rated to operate at maximum pressures equivalent to a depth of around 70 meters. We are, therefore, working to adapt the sensor to operate at high pressure. This requires repackaging the ISFET die in a rigid support structure with a proprietary process used to isolate the ISFET die substrate from solution, while still exposing the ISFET gate to the solution. Secondly, we are developing a pressure tolerant reference electrode that is stable and has a rapid response rate. Finally, we are constructing a temperature and pressure controlled facility that will allow the sensor to be tested and calibrated throughout its operating range.

WORK COMPLETED

Work to date by the partners in this project has focused on four main areas. 1) We have designed, built and begun operation of a temperature and pressure controlled (PT) test chamber that is used to assess the performance of pH sensors through a range of temperatures and pressures. 2) We have designed and constructed a Ag/AgCl reference electrode that is intended for multi-year operations. Long-term survivability of the reference electrode is now being tested through deployments on surface moorings in conjunction with the low pressure, commercially available form of the Durafet sensor. High pressure survivability is being tested by repeated pressure cycling in the PT test chamber. 3) Honeywell engineers have begun the work necessary to repackage the Durafet chip die in a simple, pressure tolerant format. This work is now focused primarily on assessing the performance of various die packaging structures and materials. We expect to begin production of encapsulated ISFET die’s near the beginning of 2011. While this design work is underway, we have adapted ISFET die’s to operate at high pressure using more common packaging techniques. These pH sensors, based on an interim packaging scheme, operate at the required pressure and temperature ranges. They have several undesirable properties, such as a distinct pressure hysteresis. They do allow us to test operation of the PT facility and to develop improved reference electrodes. The improved packaging for the ISFET die, which is underdevelopment at Honeywell, will eliminate these deficiencies. Finally, we have designed a set of electronics that will allow the completed pH sensor to operate on a profiling float. The first board set is now in production and will be delivered shortly.

RESULTS

A number of meaningful results have now been obtained. We have shown that the ISFET pH sensor has a linear temperature dependence that does not change greatly with pressure (Figure 1). We have also demonstrated that the interim design for the pH sensor has a significant pressure hysteresis signal (Figure 2). Our goal of a 0.005 pH accuracy would require pressure hysteresis effects less than 0.3 mV in Vrs (voltage reference to source). A major emphasis of the final design is elimination of this effect. We have also shown that our reference electrode design will operate through hundreds of pressure cycles and that it is stable for months in upper ocean deployments on moorings.
IMPACT AND APPLICATIONS

Economic Development
Development of a robust, accurate pH sensor that operates at high pressure will have a broad range of economic impacts that range from industrial process control, carbon storage in geological formations and carbon storage in the ocean. This is in addition to the benefit obtained from direct observations of ocean pH.

Quality of Life
The high pressure pH sensor will have direct applications to our understanding of ocean acidification and the impacts on ecosystem processes and associated economic impacts.

TRANSITIONS

Economic Development
It is our intent to develop a commercially available product for ocean observations. Our partners are currently conducting a marketing study to understand the potential implications of a robust, accurate, and pressure tolerant pH sensor in other areas.

Quality of Life
Our project will enable widely distributed observations to be made throughout the ocean interior. Such a capability would allow an observing system for ocean acidification to be developed.

RELATED PROJECTS
The overarching goal of our research is to enable global scale observing of biogeochemical properties. Related projects include the NOPP project (N00014-09-10052) to develop a commercial version of the ISUS (In situ ultraviolet spectrophotometer) for the Apex profiling float. An NSF funded project (NSF 0825348, Collaborative Research: In situ measurements of oxygen and nitrate with profiling floats deployed at ocean time-series stations) is focused on making time series observations near open ocean time-series sites near Hawaii, Bermuda, the Gulf of Alaska and in the Southern Ocean. This project will benefit when the pH sensor becomes available.

REFERENCES

PATENTS
Two patent disclosures entitled “Method for mounting electronic pH sensor die that allows high accuracy & stability during exposure to high pressure media” and “Isostatically balanced pH sensor package” have been submitted by our Honeywell collaborators.
Figure 1. ISFET pH sensor output voltage $V_{rs}$ (voltage reference to source) is plotted versus temperature for measurements near ambient pressure and at 1000 dbar pressure (equivalent to approximately 1000 m depth in the ocean). There is no significant difference in slope. Measurements were made in 0.01 mol/l HCl.

Figure 2. ISFET pH sensor output voltage versus pressure for two different sensor systems in 0.01 mol/l HCl. The results illustrate two deficiencies of the pressure package implemented at MBARI. There is significant hysteresis in the output (solid lines measured during compression and dashed lines during decompression) and sensors may have different pressure responses. That would require all sensors to be calibrated versus pressure. The pressure package under development at Honeywell is designed to eliminate these problems.