Development of an integrated ISFET pH sensor for high pressure applications in the deep-sea

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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 (year or more), in situ pH measurements in the ocean. 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

We have made significant progress towards our objective of developing a stable, pressure tolerant pH sensor that can be deployed on profiling floats. Our focus in 2010 was developing the fundamental infrastructure needed to test pH sensors at high pressure and we then began the process of developing pressure tolerant pH sensors. During 2011, we have continued designing, testing and refining high pressure pH sensors based on the Honeywell Durafet ISFET die. A number of prototype pH and reference sensor designs were developed at Honeywell and at MBARI. These designs have been tested in the laboratory high pressure test facility in order to optimize the sensor design. That work has culminated in the development of a prototype pH sensor capable of deployment in the ocean. That sensor has now been deployed multiple times to a depth of 1000 m in Monterey Bay. In addition to this work, an electronic controller capable of deployment in a profiling float was developed in 2010 and fully tested and debugged in 2011. The final software required to interface that controller with an Apex profiling float is now being completed and we expect to be able to begin deployments of pH sensors on profiling floats in early 2012.

RESULTS

Our major result in 2011 is deployment of the Deep-Sea Durafet in the ocean. The results (Fig. 1) show that the sensor can return very high quality pH measurements that have an absolute calibration based on laboratory measurements that are traceable to well defined standards. This is an oceanographic first. It has not previously been possible to calibrate an oceanographic pH sensor in the lab and then make absolute measurements in the ocean through large pressure and temperature changes due to shifts in sensor calibration. We believe that this sensor will greatly increase our ability to observe changing pH in the ocean.

Further refinement of the sensor is still required, however. For example, at this point we must calibrate the pressure coefficient of each individual sensor in the laboratory. We are working towards a design that will have a much more reproducible pressure coefficient. In order to enable a more stable design, our partners at Honeywell are implementing a highly integrated unit.

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. This is a non-trivial issue for the population of South Pacific island nations, where coral atolls form the geological base for their cities.

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

Martz, T. R., J. G. Connery and K. S. Johnson. 2010. Testing the Honeywell Durafet® for seawater pH applications. Limnology and Oceanography: Methods, 8, 172-184.

Fig. 1. pH measured in situ on a CTD/Rosette cast at stations M1 and M2 in Monterey Bay. This is the first set of deployments of a Deep-Sea Durafet sensor. The sensor was calibrated for P, T and pH response in the laboratory and no further adjustments to the data were made. The red line shows the pH measured at in situ temperature and pressure at station M1. The in situ values were then corrected to 20°C and 1 bar pressure (blue and green lines) to enable comparison to values measured in the lab at these conditions (blue and green diamonds). Corrections were made with known thermodynamic properties of dissolved carbon dioxide and borate ion in seawater using the public domain computer program CO2Sys. The agreement between pH measurements made in situ and values measured in the lab indicate that pH measurements with absolute accuracy based on laboratory calibration are possible through large P and T ranges.