Measuring pH in the Deep Ocean with Honeywell Durafet Transistors

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***Abstract*— Measuring pH in the deep ocean presents challenges in sensor stability and accuracy. The Ion Specific Field Effect Transducer (ISFET) offers significant improvements over currently available technologies. The Honeywell Durafet is an ISFET that has a history of successful pH measurement in industrial processes. Principles of pH sensing with an ISFET will be presented including a discussion of adapting the Durafet for the ocean environment. Obtaining the accuracy desired for climate studies of pH requires a complete characterization of the sensor over the oceanographic temperature range and at pressures up to 2000 decibars. The calibration process will be described and field validation data presented.**

Keywords—pH, ISFET, Durafet

I. INTRODUCTION

Measuring pH in the deep ocean has presented many challenges in sensor stability and accuracy. The Ion Specific Field Effect Transistor (ISFET) offers significant improvements over currently available technologies. The Honeywell Durafet is an ISFET that has a history of successful pH measurement in industrial processes and has been adapted for use in the deep ocean. The principles of pH sensing with an ISFET will be presented including a discussion of adapting the Durafet for the ocean environment.

The ISFET measurement technique is described in detail in Bergveld [1] and ISFET application to pH sensing in seawater is discussed in Martz [2]. Briefly, an ISFET is type of MOSFET. A MOSFET will conduct electrical current depending on the voltage on the gate terminal. An ISFET differs in that the gate terminal is replaced by an ion sensitive material, in the case of the Durafet the gate is sensitive to the concentration of H^+ ions.

An ISFET pH sensor exposes three components to seawater. The first is the pH sensitive area of the ISFET. The second, the counter electrode, is used to create a small electrical field which causes the ISFET to conduct a constant current. The third, the reference electrode, is a chloride Ion Specific Electrode (ISE) that develops a voltage that is proportional to the concentration of chloride ions, Cl^- in the seawater. As with all electrochemical processes this can be described as two half cells, one half is the ISFET and counter electrode, the other is the AgCl chloride ISE. These half cells share a common ground and the voltage that develops on the ISE is the signal that is proportional to the pH of the seawater being measured.

Figure 1 is a representation of the circuits used to create a constant current through the ISFET and to measure the voltage that is present on the reference electrode. The drain, source, pH sensitive gate material and the counter electrode are labeled in the drawing. Note that there is a feedback portion of the circuit that is omitted for clarity. Figure 2 shows the ISFET probe on the left and the counter electrode / ISE reference electrode on the right, the counter electrode is the metal ring that surrounds the ISE and the ISE is the dark disk at the top.

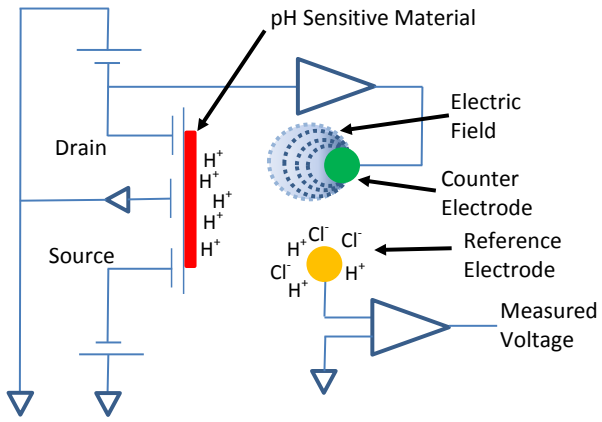

Fig. 1. Schematic representation of ISFET, Counter Electrode and Reference ISE and operating components.

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Fig. 2. ISFET, center of probe on left. Counter electrode, ring around probe on right. ISE, dark top part of probe on left.

When it is operating, the ISFET conducts a feedback controlled constant current from drain to source that depends on both the concentration of H^+ ions and the electrical field created by the voltage on the counter electrode. The reference electrode exhibits a linear (Nernstian) response to chloride activity and the measured voltage of the reference electrode is proportional to the activity of H^+ and Cl^-, relevant equations are shown below.

$$pH = -\log(a_{H^+}) = -\log(\gamma_{H^+}[H^+]) \quad (1)$$

a_{H^+}= Activity of H^+
γ_{H^+}= Activity coefficient for H^+
$[H^+]$ = Concentration of H^+ (molality; mol kg-H_2O^{-1})

Equation (1) is the relationship between pH and H^+ concentration. The activity of H^+, aH^+, is the concentration of H+ that is available to interact with the sensor. This is expressed as the activity coefficient, gamma, multiplied by the true concentration of H^+. Gamma has a value less than one and depends on temperature. For fresh water the activity coefficient is very close to one and pH is directly related to the concentration of H^+. Equation (2) is the relationship that is used to calculate pH from the measured reference ISE voltage.

$$E_m = E_{ref} - \frac{RT\ln(10)}{F}\log(\gamma_{H^+}[H^+]) - \frac{RT\ln(10)}{F}\log(\gamma_{Cl^-}[Cl^-]) \quad (2)$$

In equation (2), Em is the measured reference electrode voltage, RTln(10)/F is the ideal Nernstian slope (S), $[H^+]$ and $[Cl^-]$ are the concentrations of H^+ and Cl^- respectively and Eref is a correction term for non-ideal behavior over the temperature and pressure range of the ocean. Equation (3) is an expansion of Eref showing the temperature and pressure correction functions.

$$E_{ref}(T,P) = k0 + k2 \times T + f(P) + \frac{-\bar{V}_{Cl}P + 0.5\bar{\kappa}_{Cl}P^2}{10F} \quad (3)$$

II. Calibration Theory

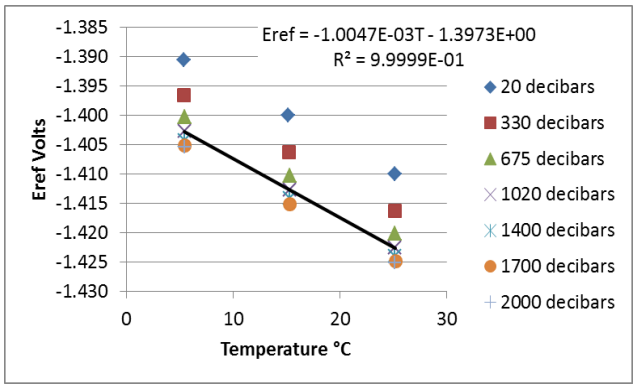

Fig. 3. ISFET slope sensitivity over the oceanographic temperature range.

Eref is a function of temperature and pressure with coefficients determined in calibration. The offset term, k0 is dependent on the condition of the reference ISE, it is measured in the laboratory after the sensor has equilibrated to the chloride and bromide concentration in seawater. This process is typically done after the sensor has finished temperature and pressure calibration and will be discussed after these procedures are described. The linear temperature term, k2, compensates for the change in response of the sensor over the oceanographic temperature range. Figure 3 shows the sensor response of an example probe, k2 is the slope of the linear fit to the 1020 decibar data.

Because there is a small pressure effect on the slope of these response curves a value for k2 is chosen at the mid-point in the calibration range of 1000 decibars. The pressure effect on offset is considered below.

The pressure compensation function F(P) is a fourth order polynomial, Figure 4 shows typical Durafet pressure response that is well described by the fourth order equation.

The fourth term in equation (3), Eref compensates for the molal contraction of the working fluid in the calibration apparatus or seawater when the sensor is used in the field. This relationship is described in Byrne and Laurie [3], the authors state that the portion of the relationship that depends on P^2 is very small allowing this term to be dropped in the final calculation.

Calibration of the offset term, k0, must be done in seawater. The process is described in Bresnahan [4]. Briefly, the process consists of exposing the reference ISE to seawater and allowing the chemical substitution of bromide ions for chloride ions in the solid silver/silverchloride material that makes up the sensitive portion of the electrode. Because this ion substitution occurs in a solid material it is a slow process that can take up to 10 days to reach equilibrium.

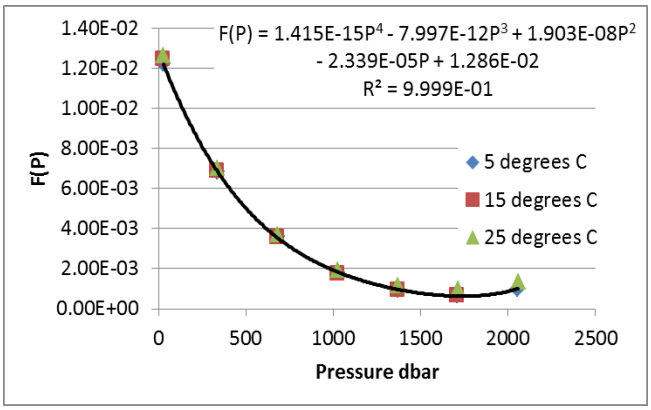

Fig. 4. ISFET response to pressure.

III. Calibration Apparatus

Evaluating the terms in Eref that serve as a correction for non-ideal behavior requires calibrating the ISFET and ISE reference electrode in a solution with known thermodynamic properties. A dilute solution of hydrochloric acid has thermodynamic properties that are well documented and serves as the working fluid in the calibration apparatus shown in Figure 5.

Figure 5 shows the pressure / temperature calibration vessel. The probes are currently calibrated over the range of 5 – 35 degrees C and 0 – 2000 decibars making a matrix of 4 temperature points and 7 pressure points. Temperature control is supplied by a recirculating chiller plumbed to manifolds on each side of the pressure vessel and pressure is supplied by a syringe pump. The apparatus holds three probe pairs, these can be seen as the large fittings on the front with wires that lead to a connecting block, one half of the pair in the front, the other half in the back.

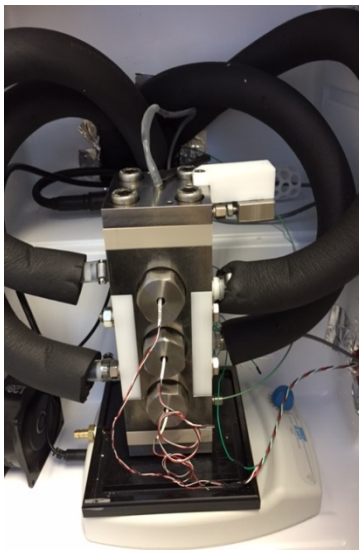

Fig. 5. Calibration apparatus, used to calibrate probes over oceanographic temperature and pressure range.

IV. Calculating pH

To calculate pH from the reference electrode voltage temperature and pressure must be known to correct the sensor output for non-ideal behavior using the coefficients described above and salinity must be known to calculate the chloride ion concentration using the relationship described by Millero [4]. Rearranging equation (2), equation 4 is used to calculate pH.

$$pH = \frac{\left(E - E_{ref}\,(T,P)\right) + S \times 2 \times \log(\gamma_{HCl}) + S \times \log([Cl^-])}{S} \quad (4)$$

Where $S = \frac{RT\ln(10)}{F}$

V. Field Validation

The Deep Sea Durafet (DSD) was tested in May of 2015 at the Hawaii Ocean Time series ALOHA station; this site has been occupied monthly for over two decades with pH measurements being made at discrete depths for each cruise. Figure 6 shows pH data for the spring of 2014 plotted along with DSD profile of total *in-situ* pH measured in May 2015.

DSD surface measurements are higher than station ALOHA historic data by 0.04, this artifact does not appear to be equilibration of the probe because both down and up casts exhibit the same offset which is shown in detail in figure 7. Figure 7 is the first five minutes of the cast plotted with the last five minutes of the cast. After an initial two minute equilibration of the reference electrode the down and up casts agree well demonstrating minimal hysteresis.

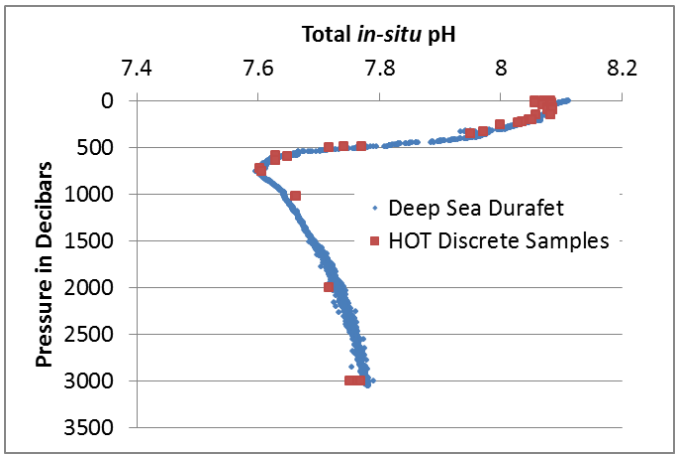

Fig. 6. Field validation of ISFET at Hawaii Ocean Time series station ALOHA.

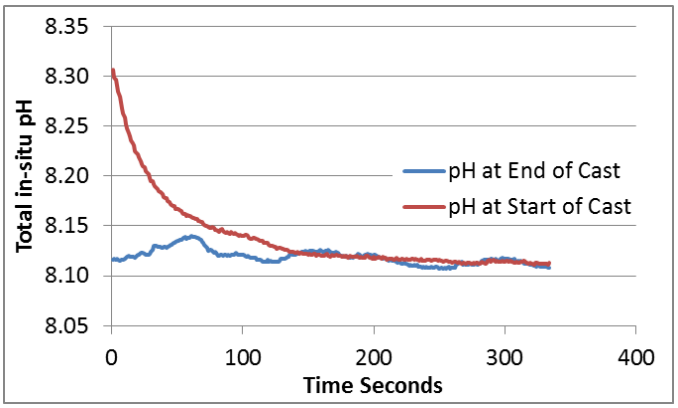

Fig. 7. Starting five minutes and ending five minutes of 1000 decibar profile.

DSD response time is in the range of 5 to 8 seconds and is estimated by advancing up and down profile data referenced to pressure to remove hysteresis. Figure 8 shows a waterfall plot of an example cast with no pH advance, 5 seconds and 8 seconds respectively. The optimal advance will match up and down cast and is approximately 8 seconds.

VI. Conclusion

The Deep Sea Durafet has demonstrated stability and accuracy in its initial field testing and with some work to improve manufacturability promises to provide reliable pH measurements for oceanographic applications. Reasonably fast response time and low hysteresis will allow the sensor to be used in profiling applications as well as for moored time series.

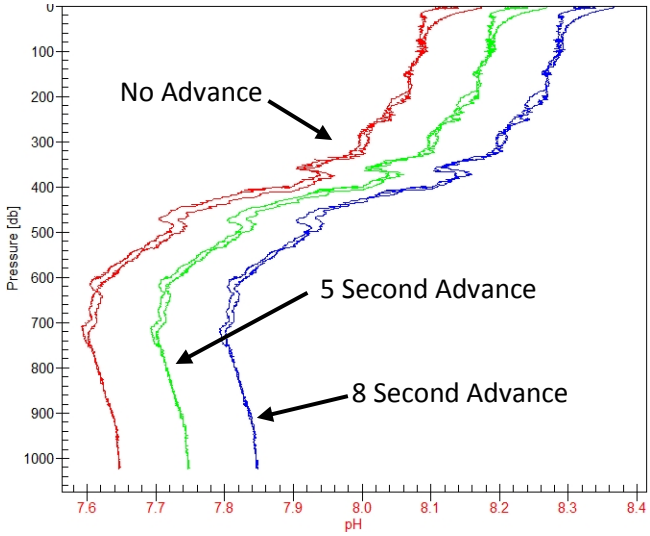

Fig. 8. Waterfall plot of 1000 meter profile of pH showing the results of advancing pH relative to pressure.

Acknowledgment

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References

[1] P. Bergveld, "Thirty years of ISFETOLOGY. What happened in the past 30 years and what may happen in the next 30 years", Sensors and Actuators B 88, pp. 1–20, 2003.

[2] T. R. Martz, James G. Connery, and Kenneth S. Johnson, "Testing the Honeywell Durafet® for seawater pH applications", Limnol. Oceanogr.: Methods 8, pp. 172–184, 2010.

[3] R. H. Byrne and S. H. Laurie, "Influence of Pressure on Chemical Equilibria in Aqueous systems – with Particular Refrence to Seawater", Pure Appl. Chem., Vol. 71 No. 5 pp. 871-890, 1999.

[4] P J. Bresnahan Jr., T. R. Martz, Y. Takeshita, K. S. Johnson, M. LaShomb, "Best practices for autonomous measurement of seawater pH with the Honeywell Durafet", Methods in Oceanography 9, pp. 44–60, 2014.

[5] F. Millero, "Influence of Pressure on Chemical Processes in the Sea", Chemical Oceanography, Vol. 8, 1983.