

## ***Interactive comment on “Electrochemical techniques and sensors for ocean research” by G. Denuault***

**Prof Luther (Referee)**

luther@udel.edu

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This is overall a balanced review on all types of electrochemical sensors and methods with emphasis on real time measurements. The author first describes the types of sensors, their general principles of measurement and then he reviews some applications to ocean science. He also gives ideas for future developments that would encourage others to use these techniques and to improve their efficiency for use by electrochemists and non-electrochemists alike. I agree that for multi-analyte sensors in particular, such as voltammetry, data reduction methods should become more rapid and robust.

Because the author also writes for non-electrochemists, I thought that another figure or two could be included that would expand on Table 2 and show the relationships between the various techniques better. For example, the author could show the var-

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ious excitation signals over time along with the measurement parameter (I, E, Q, Z) and the relationship of the measuring signal to concentration or activity. I also thought that equations could be used to show how I, E, Q, Z relate to concentration or activity and that the relationship between concentration and activity could be explicitly stated. These additions would help in the stated objectives on page 1859 that these sensors “...are limited more by the lack of expertise...” that most researchers have in electrochemical methods.

On page 1870 lines 5-15, the author discusses hysteresis for membranes covering sensors. A paper that describes a comparison for oxygen determination using both optodes and Clark type sensors versus Winkler titrations and voltammetry is Glazer, B. T., A. G. Marsh, K. Stierhoff and G. W. Luther III. 2004. The dynamic response of optical oxygen sensors and voltammetric electrodes to temporal changes in dissolved oxygen concentrations. *Analytica Chimica Acta* 518, 93-100.

The author generally does a good job of referencing previous reviews and papers that adequately describe the specific techniques. An omission I noticed was that the author did not reference recent hydrothermal vent work using electrochemical techniques especially at high temperatures. These are significant technological advancements and include the pH, H<sub>2</sub> and H<sub>2</sub>S measurements of Ding and Seyfried as well as the conductivity sensor of Larson et al which is a proxy for chloride as sulfate is in low concentration in hot vent waters. Le Bris et al have also developed a pH probe for diffuse flow vent lower temperature work. All these were briefly reviewed in Moore et al.

Ding K, Seyfried WE. 2007. In situ measurement of pH and dissolved H<sub>2</sub> in mid-ocean ridge hydrothermal fluids at elevated temperatures and pressures. *Chemical Reviews* 107: 601-22.

Ding K, Seyfried WE, Tivey MK, Bradley AM. 2001. In situ measurement of dissolved H<sub>2</sub> and H<sub>2</sub>S in high-temperature hydrothermal vent fluids at the Main Endeavour Field, Juan de Fuca Ridge. *Earth and Planetary Science Letters* 186: 417-25.

Larson BI, Olson EJ, Lilley MD. 2007. In situ measurement of dissolved chloride in high temperature hydrothermal fluids. *Geochimica Cosmochimica Acta* 71: 2510-23.

Le Bris N, Sarradin PM, Pennec S. 2001. A new deep-sea probe for in situ pH measurement in the environment of hydrothermal vent biological communities. *Deep-Sea Res. Part I-Oceanogr. Res. Pap.* 48:1941–51.

Moore, T. S., K. M. Mullaugh, R. R. Holyoke, A. S. Madison, M. Yücel and G. W. Luther, III. 2009. Marine Chemical Technology and Sensors for marine waters: Potentials and Limits. *Annual Reviews in Marine Science* 1, 91-115.

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