

## Development of a Long-Range Underwater Vehicle

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### LONG-TERM GOALS

Our overall goal is to increase the capabilities of today's long-range Unmanned Underwater Vehicles (UUVs) and Unmanned Underwater Gliders (UUGs) by using high-energy-density lithium-seawater batteries. Specific objectives are (1) to test in the laboratory and ocean new lithium-seawater batteries developed and manufactured by the PolyPlus Battery Company, (2) to discover how to mount and operate these cells to minimize adverse impacts of limited mass transfer with the ambient seawater and of bio-fouling, and (3) to develop a long-range underwater UUV or UUG to exploit this energy source. Our target is to double the range/duration of long-range neutrally buoyant underwater vehicles.

### OBJECTIVES

Based on reaction energy and reactant mass, oxidation of lithium is particularly attractive for high energy-density batteries. Each gram of lithium can supply 3.8 A hr of current at a voltage that depends on the reaction leading to lithium oxidation. The no-load potentials of the primary lithium-oxygen and lithium-water couples likely in seawater are

Oxygen reduction in seawater       $4\text{Li} + \text{O}_2 + 2\text{H}_2\text{O} = 4\text{LiOH}$        $E \sim 3.45\text{ V}$

Hydrogen evolution in seawater       $2\text{Li} + 2\text{H}_2\text{O} = 2\text{LiOH} + \text{H}_2$        $E \sim 2.60\text{ V}$

The theoretical energies per unit mass of reactant of these reactions are  $13.3\text{ W hr kg}^{-1}$  ( $49\text{ MJ kg}^{-1}$ ) and  $9.9\text{ W hr kg}^{-1}$  ( $36\text{ MJ kg}^{-1}$ ), respectively.

The PolyPlus Battery Company has developed and patented a unique lithium-seawater battery (<http://polyplus.com/liwater.html>) suitable for underwater vehicles that approaches the theoretical energy densities for oxygen and hydrogen evolution. Each cell uses a Protected Lithium Electrode in which the lithium anode is separated from seawater by a "solid electrolyte" membrane that passes lithium ions but not water molecules. The new battery, which combines this pressure compensated anode with a cathode optimized for oxygen reduction, is operated in ambient seawater at ocean depths.

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PolyPlus has tested these cells under laboratory conditions with excellent performance and have achieved energy densities (energy delivered per unit of pre-discharge battery mass) near 4.7 MJ/kg, four times the energy density available from the most powerful lithium primary batteries used in floats and gliders today. The seawater cells are also substantially safer than high power batteries now in use.

The objectives of the full project are to:

1. to test PolyPlus lithium-seawater cells in the field to define their capabilities for powering marine vehicles and sensors;
2. to design and build a prototype long-range underwater vehicle to exploit the new energy source; and
3. to report the performance advantages and limitations of lithium-seawater batteries based on field tests of the prototype vehicle.

With first-year funding we are addressing only the first objective.

## **APPROACH**

Russ Davis and Jeff Sherman of Scripps are collaborating with Steve Visco and Eugene Nimon of PolyPlus on this work. Visco, founder and CEO of PolyPlus, and Nimon, the Director of Research and Development there, are essential technical resources for planning and interpreting tests of the lithium-seawater batteries; PolyPlus also provides batteries for testing. Sherman and Davis, who developed the Spray glider and several other ocean technologies, will design and build test facilities, carry out field tests, and head up design and construction of the prototype vehicle.

The general approach for the testing phase is to characterize performance of the batteries in laboratory tests and then carry them to sea for multi-month missions as “passive passengers” on Spray gliders. Laboratory tests (like pressure cycling and measuring cell performance under different electrical and hydrodynamic conditions) provide a well controlled environment while field missions expose the cells to realistic conditions and biological fouling.

In the battery testing phase, specific issues are (a) confirming that the anodes are not harmed by pressure cycling, (b) learning how to provide adequate mass transfer between the cell electrodes and seawater so that cell voltage is not greatly reduced by depleted reactant concentration or precipitate formation on the cathode, and (c) exploring ways to minimize biofouling around the cells that could decrease mass transfer. Laboratory pressure tanks are suitable for pressure cycling and mass transfer is measured in a laboratory facility where individual cells are moved through quiescent seawater. Cell performance under ocean conditions is measured by connecting them to different electrical loads as their host Spray glider records voltage and current while cycling vertically to expose the cells to different oxygen and temperature environments. The field tests are long enough to permit substantial biofouling, which is characterized by post-cruise examination.

The major design issues are (a) comparing battery suitability for powering UUVs driven by propellers and for UUGs that use buoyancy change for propulsion, (b) providing peak power from seawater batteries that are best operated continuously near their average power and cannot be connected in series to increase operating voltage, (c) achieving good mass transfer without an excessive vehicle-drag penalty, and (d) taking advantage of the vehicle size and weight savings made possible by batteries that

operate in ambient seawater. These will be approached through engineering design, computer simulation with simple models, and laboratory tests to measure mass transfer and drag.

## WORK COMPLETED

Pressure cycling of Protected Lithium Electrodes has been carried out, followed by microscopic examination of the electrodes and performance testing.

Performance of individual cells has been measured as they were moved through quiescent seawater at a range of speeds in our laboratory seawater tank. This provides a reference for comparison with the effects of mass transfer achieved on vehicles under ocean conditions.

Two Spray missions with PolyPlus cells have been carried out off the California coast. The first exposed aspects of cell behavior not accounted for the test design, leading to redesign of the test apparatus and procedure. A second test of two additional cells lasted 69 days covering 729 dives, most to 400 m. Ocean temperature, salinity and oxygen profiles were measured with an SBE41CP CTD and an SBE43F oxygen sensor. This test provided high-quality performance data under a range of operating and environmental conditions and an opportunity for significant biofouling.

## RESULTS

Pressure cycling to 1600 decibar in the laboratory and field to 400 decibar produced no evident performance degradation or visible damage to the Protected Lithium Electrode. This electrode, when mounted as the anode in a cell, is reasonably rugged and adequately robust for normal handling. The cell cathode, which is a thin layer of a fibrous weave, is easily distorted by handling or field use; a stronger support is needed.

As a reference for mass-transfer rates in field studies, battery output was measured as cells were moved through quiescent seawater saturated with oxygen in a laboratory tank. At current densities less than  $0.6 \text{ mA/cm}^2$  velocity changes over the range 5 to 12 cm/s changed cell voltage by only O(1%). Thus with well-oxygenated waters and typical Spray velocities around 30 cm/s direct problems from hydrodynamical mass transfer should be minimal. The cell reactions produce LiOH and raise pH, potentially precipitating seawater salts onto the cathode and significantly reducing mass transfer and cell output. No such precipitates were observed at current densities below  $0.6 \text{ mA/cm}^2$  and 3.5 to 12 cm/s velocities, but the laboratory tests were only hours long.

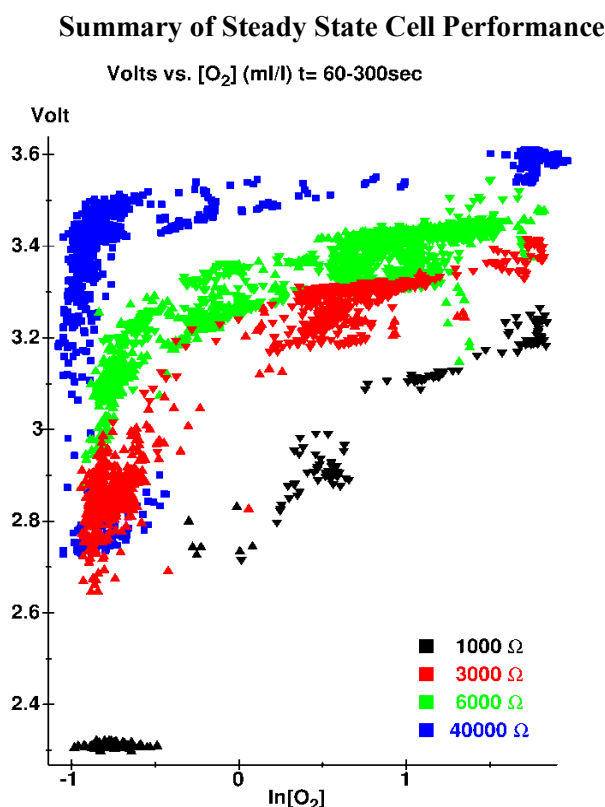
An unexpected finding in both laboratory and field tests is that cells exhibit an O(30 sec) time constant in responding to electrical load changes. This is orders of magnitude greater than the overall cell hydrodynamic flushing time ( $L/U$ ), but flushing of the woven-mat cathode is probably much slower.

For field trials two lithium-seawater cells were mounted below Spray's tail section. Because the wing, which needs an angle of attack to produce lift, is aligned with the hull, mass-transfer to the cells was poorer during ascent than in descent. At the field site,  $\text{O}_2$  concentration was 100% saturated ( $5.7 \text{ ml l}^{-1}$ ) near the surface, declined to 50% over the upper 50 m, and declined to 10% by 400 m. Electrical-load changes, most of which were made below 50 m where  $\text{O}_2$  was significantly depleted, had two characteristics that differed qualitatively from the observed laboratory behavior. First, cell output for a given load was lower than in the laboratory tests by substantially amounts that significantly exceeded the thermodynamic effect of ambient  $\text{O}_2$  concentration on cell open-circuit voltage. Second, the time

for the cell potential to equilibrate to a load change frequently increased substantially, sometimes to O(10 minutes). Both these effects were strongest when the load was heavy, oxygen concentration was low or ascent had reduced mass transfer.

The combination of factors that minimized cell voltage and maximize the response time in the field makes it clear that mass transfer was becoming inadequate to supply the oxygen needed to support higher currents. The extreme of this occurred when current density increased to  $0.6 \text{ mA cm}^{-2}$  during ascent. Cell voltages declined to 2.3 V and their variability dropped from 0.1 V to around 0.01 V. Evidently poor mass transfer forced  $\text{O}_2$  concentration on the cathode to become so low that the electrode reaction shifted from oxygen reduction to hydrogen evolution.

Surprisingly, as the field-trial cell potentials varied in complex and seemingly erratic ways by O(1 V), the equilibrated voltages of the two cells differed by less than 2.5 mV. Evidently the large variations were reproducible responses to the environment, not to factors like pressure-cycling damage or biofouling that would affect individual cells.



**Figure 1. Steady-state cell voltage is plotted against the natural log of dissolved oxygen concentration ( $\text{ml l}^{-1}$ ) for four color-coded loads (ohms). There are three performance regimes. At high  $[\text{O}_2]$ , O(100 mV) noise overlies a gradual downward voltage trend as  $[\text{O}_2]$  decreases. As  $[\text{O}_2]$  decreases further there is a clear transition to a steep  $V$  vs  $\text{O}_2$  relation. At higher current density the transition occurs at higher  $[\text{O}_2]$  and the  $V$  vs  $\text{O}_2$  slope decreases. The cluster of low-oxygen points for 1 kΩ load shows a stable cell voltage of 2.3 V. The cell has switched to the hydrogen evolution reaction, which is unaffected by  $[\text{O}_2]$  and by the process adding voltage noise to the oxygen reaction.**

Figure 1 summarizes the equilibrated cell voltage as a function of oxygen concentration for four different loads and current densities of 10 to 300  $\mu\text{A cm}^{-2}$ . This shows a transition from a gradual voltage trend with  $[\text{O}_2]$  to a steep drop of voltage as  $[\text{O}_2]$  decreases. This transition marks substantial depletion of oxygen at the cathode from the combination of low ambient  $[\text{O}_2]$  and “concentration polarization” when mass transfer cannot supply the oxygen needed to support the cell current. The cluster of low  $\text{O}_2$  points with stable voltage near 2.3 V mark a change of cell reaction from oxygen reduction to hydrogen evolution.

Visual inspection after the 69-day field test indicated substantial biofouling around the electrode support structure in the batteries and less, but still substantial, biofouling of the both electrodes. The most robust forms, found even between the electrodes, were immature barnacles whose “foot” sometimes approached the cell dimensions. Hair-like forms were also found.

Apparently inorganic structures resembling stalagmites and stalagmites were found between the electrodes; a few of these connected the electrodes. Their morphology and friability suggest these are precipitates caused by high-pH reaction products from the cathode. This is supported by discovery of significant quantities of similar material imbedded in the weave of the cathode. We conclude that even at current densities well below 1  $\text{mA cm}^{-2}$ , the mass transfer rates achieved in the field were inadequate to flush high-pH reaction products from the cell, particularly the cathode mat.

Our main result is evidence that the PolyPlus lithium-seawater cells performed well in the field, particularly in well oxygenated surface waters. Oxygen starvation led the cell to shift to the lower-voltage hydrogen evolution reaction for which the main reactant, water, is unlimited. Despite apparent biofouling and accumulation of precipitates in the batteries, there was no clear evidence of performance degradation over 69 days in very biologically rich waters.

We conclude that future tests should focus on the feasibility of operating cells in order to use both the oxygen reduction and hydrogen evolution reactions, depending on the availability of oxygen and the current density needed.

## **IMPACT/APPLICATIONS**

The capabilities of sensor systems on various autonomous ocean-observing vehicles and the sustained speed and range of those vehicles are all directly proportional to the energy density of the vehicle’s power source. Because lithium-seawater batteries potentially provide such a large increase in energy density, studies of the performance that can be achieved in the ocean, and of ways to maximize it, are central to the evolution of long-term scientific and Navy ocean observing systems.

## **RELATED PROJECTS**

We are unaware of any related projects. PolyPlus is, of course, involved in extensive proprietary research on the lithium-seawater battery and other types of battery (<http://polyplus.com>).