24 Hour Test of a Fuel Cell System for an Autonomous Underwater Vehicle

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The Norwegian Defence Research Establishment (FFI) has a long experience with power sources for autonomous underwater vehicles (AUVs). FFI has designed and built a power supply system based on a water-cooled and air-supplied PEM fuel cell stack from Ballard. Hydrogen is supplied from a pressure tank, while oxygen is produced by catalytic decomposition of industrial grade hydrogen peroxide. Excess hydrogen is catalytically combined with oxygen in the internal atmosphere of the pressure hull. The fuel cell system is fully automated and self-regulating according to the set current. A 24 hour continuous test of the system was conducted in a sealed pressure hull under water. The system showed stable and reliable performance throughout the test, with only a small and recoverable voltage decrease.

Introduction

The Norwegian Defence Research Establishment (FFI) has been working with power sources for autonomous underwater vehicles (AUVs) for more than two decades. In cooperation with Kongsberg Maritime, Statoil and Norwegian Underwater Intervention (formerly NUTEC), FFI developed the HUGIN AUV, which is dominating the market for subsea survey AUVs [1]. Kongsberg Maritime is the commercial manufacturer of the HUGIN AUV [2], which is one of several classes in the Kongsberg Maritime AUV family that also includes portable systems and gliders.

FFI has developed several power sources for AUV, including sea water batteries [3], aluminum/hydrogen peroxide (Al/HP) semi fuel cells [4] and pressure tolerant Li-ion batteries [5]. To facilitate an extended operating range, FFI has also developed an air independent fuel cell system for AUV. This paper describes the fuel cell system and a 24 hour test that was carried out to verify its performance.

Fuel cell powered AUVs have been demonstrated before [6, 7], but are still not commercialized. Further development, especially on storage of oxidizer and fuel, is needed before fuel cells can outperform batteries or Al/HP semi fuel cells.

Challenges for fuel cell systems on AUVs

A fuel cell system roughly consists of four sub-systems: fuel cell with balance of plant, electronics (including buffer battery and DC/DC converter), fuel and oxidizer. Compared to most "normal" open air systems, only the electronics stay unchanged when entering the ocean on board an AUV.

The most obvious constraint for an AUV fuel cell system is the *absence of air*, which means the energy system needs to include an oxidizer in addition to the fuel. This will lower the energy density compared to terrestrial systems and gives batteries an edge over fuel cell systems. To be competitive, both oxidizer and fuel storage (and potentially conversion) system need to be compact. There are several possible solutions [8], where all have their pros and cons – much dependent on the intended use.

Fuel and oxidizer can be stored as gas in high pressure cylinders, cooled as liquid, bound as a chemical substance or produced on demand from a chemical reaction. The aim when selecting storage and generation method is to obtain the highest volumetric and gravimetric energy density, while retaining neutral buoyancy for the AUV as a whole. Pressure cylinders ensure a simple system and are well suited for increasing the buoyancy, but are bulky. Liquid oxygen (LOX) has by far the highest gravimetric and volumetric oxygen density of possible oxidizers, but is complex and less favorable for small AUVs designed for deep diving. Chemically bound oxidizers and fuel can be stored very compact. Depending on the method, they could both need a conversion system and give by-products that must be discharged from the AUV.

The AUV fuel cell system must be operated in a pressure hull to protect it from the surrounding sea water. Product water from the fuel cell and by-products from any oxidant or fuel conversion must be removed to minimize the needed pressure hull volume. This demands systems that will add weight and complexity. The amount of gaseous impurities in the reactants should be very small when operating in a pressure hull, as they are not easily removed.

The list of challenges also includes safety issues, change in ballast and trim, controlling relative humidity and temperature in the pressure hull, and more. In addition, the fuel cell system must work autonomously for days and handle unforeseen incidents.

Description of FFI's fuel cell system

The fuel cell system is based on a PEM fuel cell stack from Ballard (9SSL V4). This stack is not designed to operate on pure oxygen, which is defining our principal approach. Figure 1 shows a schematic of the system, built into an AUV. The vessel hull protects the interior of the AUV against mechanical damage and reduces drag, but is open to the ambient sea water. All sensitive equipment, including the fuel cell, oxygen generator and electronics, must be placed inside a sealed pressure hull to protect it from the ambient sea water and pressure.

Hydrogen is supplied from a pressure tank outside the pressure hull. Alternative storage concepts, such as methanol reforming or metal-water reactions, are also considered. The hydrogen feed is regulated to maintain the anode pressure, and a recirculation pump ensures constant flow of hydrogen through the anode. To avoid cell voltage drop, about 1 % of the supplied hydrogen is purged out of the stack and into a hydrogen processing unit where it is combined with oxygen before fed to the internal atmosphere of the pressure hull.
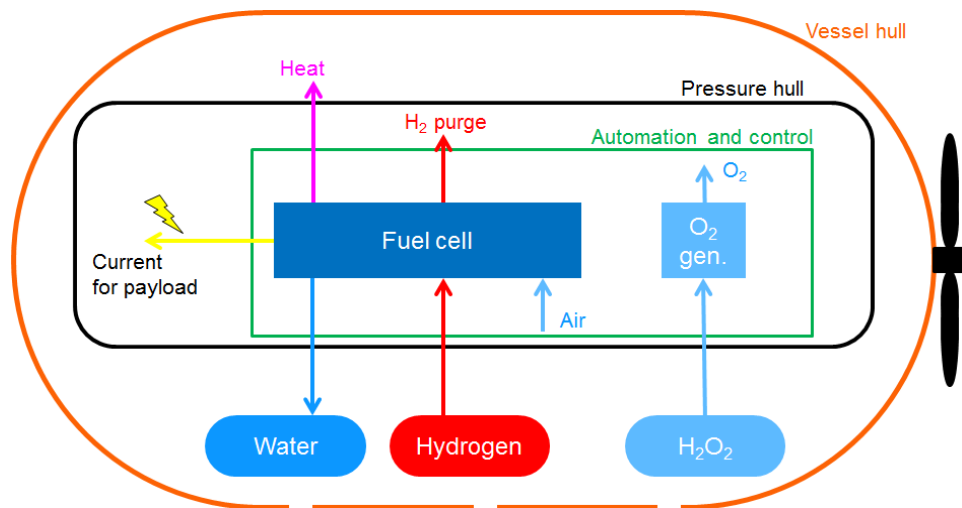
Figure 1.   Schematic lay-out of the fuel cell system

Oxygen is produced on demand and fed to the internal atmosphere of the pressure hull. While air from the pressure hull is supplied to the fuel cell, this maintains a constant oxygen concentration. Oxygen is produced by catalytic decomposition of industrial grade hydrogen peroxide in an oxygen generator. Hydrogen peroxide is a liquid and can be stored outside the pressure hull in a flexible plastic container. It is pumped into the reactor where it is converted to oxygen and water. Water is removed from the oxygen flow in a 0.4 MPa buffer tank and a filter removes impurities that are associated with industrial hydrogen peroxide. Oxygen is then mixed with the cathode outlet stream and fed to the pressure hull.

Product water, both from the fuel cell reaction and the oxygen generator, is collected in a rigid water container outside the pressure hull. A part of this water must be pumped to the ambient in order to maintain neutral buoyancy as hydrogen and hydrogen peroxide is being consumed.

Cooling water is supplied to four heat exchangers: cooling fan in the pressure hull, oxygen cooler, exhaust air cooler and stack cooler. The stack is cooled by deionized water in a separate cooling loop.

The fuel cell stack current is controlled by an electronic load. The system is controlled and fully automated using National Instruments LabView[TM] and Compact FieldPoint. The system starts automatically and is self-regulating according to the set current.

The fuel cell system is mounted in a rack as shown in figure 2. In one end it has an end-plate with subsea connectors for reactants, power and signals. The rack is equipped with wheels and can slide into the pressure hull.
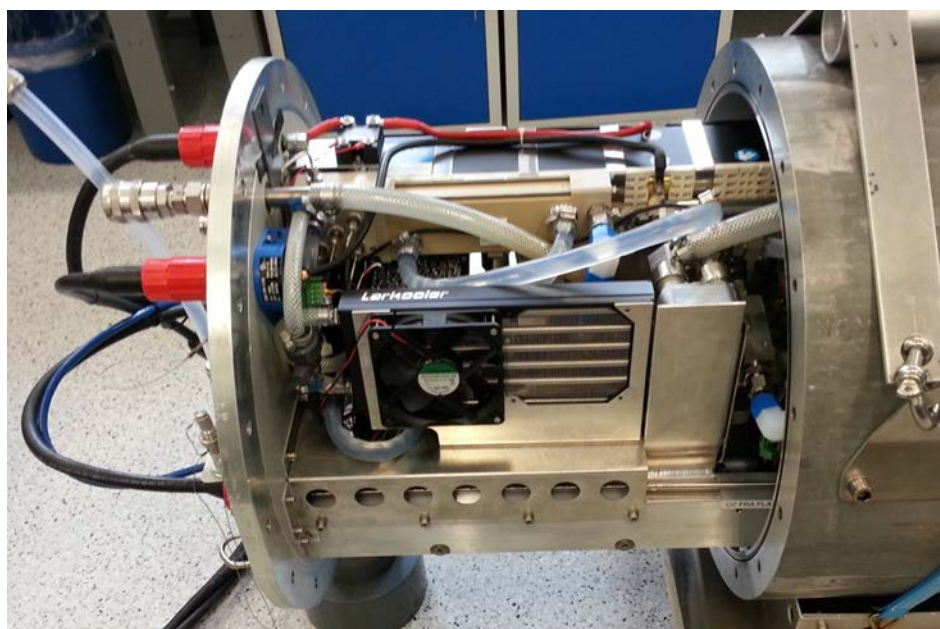
Figure 2: Fuel cell system sliding into the pressure hull

Without using the pressure hull, the layout also makes it easy to emulate a closed container by simply covering the rack with a plastic sheet, thus forming a semi-closed compartment. This has enabled us to study the system's ability to control hydrogen leakage, oxygen concentration, humidity and temperature, as well as circulation of gases in the pressure hull. However, pressure changes, build-up of inert gases and the thermal interface are not representative in this set-up.

Analysis of produced oxygen

Oxygen is produced from hydrogen peroxide of T49.5 industrial grade, which has a distinct organic odour. Since the produced oxygen gas had a similar smell during the initial tests of the oxygen generator, an analysis was conducted to determine the composition of the gas. The goal was to design a filter system – on basis of the analysis – to remove substances that potentially could be harmful to the fuel cell. In addition, inert impurities added to the sealed pressure hull would over time raise the pressure to undesirable levels.

There are several possible sources of contamination in hydrogen peroxide T49.5 grade, and many of them stem from the production [9]. M. Kogure et. al [10] suggest that formic acid and acetic acid are the main impurities in hydrogen peroxide. However, their experimental method implies that these substances could be products of other chemicals. Carbio et. al [11] conclude that the amount of total organic carbon in semiconductor grade hydrogen peroxide could be as much as tenths of ppm. However, as M. J. Camenzind [12] points out, organic contaminations in hydrogen peroxide are difficult to measure as hydrogen peroxide must be decomposed before analysis in order to protect the instruments.

Analysis of the oxygen gas was performed with Fourier Transform Infrared Spectroscopy (FTIR) and Dräger tubes. Based on the analysis, a filter was developed to remove the impurities, followed by analysis of the purified gas.

Analysis with FTIR

FTIR analysis was conducted with Gasmet DX4015 with accompanying software. The sample gas was flushed through an Erlenmeyer flask connected to the Gasmet until stable values were reached. The resulting spectrum from the analysis is shown in Figure 3 and 4. Water is evident in both figures as noise in areas 1200-2100 and 3300-4100 cm^{-1}, while CO_2 is the big dip at 2300 cm^{-1}.

Figure 3 shows the FTIR spectrum of unfiltered, moist oxygen (upper) and water (lower). In spectrums shown in this paper the background signal (air) is subtracted, leading to negative absorption values for substances not containing the same amount as in the background, such as CO_2 and water. The spectrum from the produced oxygen has three more or less distinct areas that separate it from the spectrum of water. A) Very strong peaks between 2600 and 3000 cm^{-1}, which is typical for single C-H-bonds and indicates hydrocarbons. B) 1680-1730 cm^{-1} is less clear, but points towards a C=O-bond. According to Solomons [13], the area applies very well for aldehydes and ketons, but less for esters, eters, alcohols, amids, carboxylic acid and hydrocarbons with chains of more than four $-CH_2-$ and rules out cyclic hydrocarbons. C) The area between 800 and 1200 cm^{-1} is sometimes possible to compare with a good library of compounds, but no matches were found.
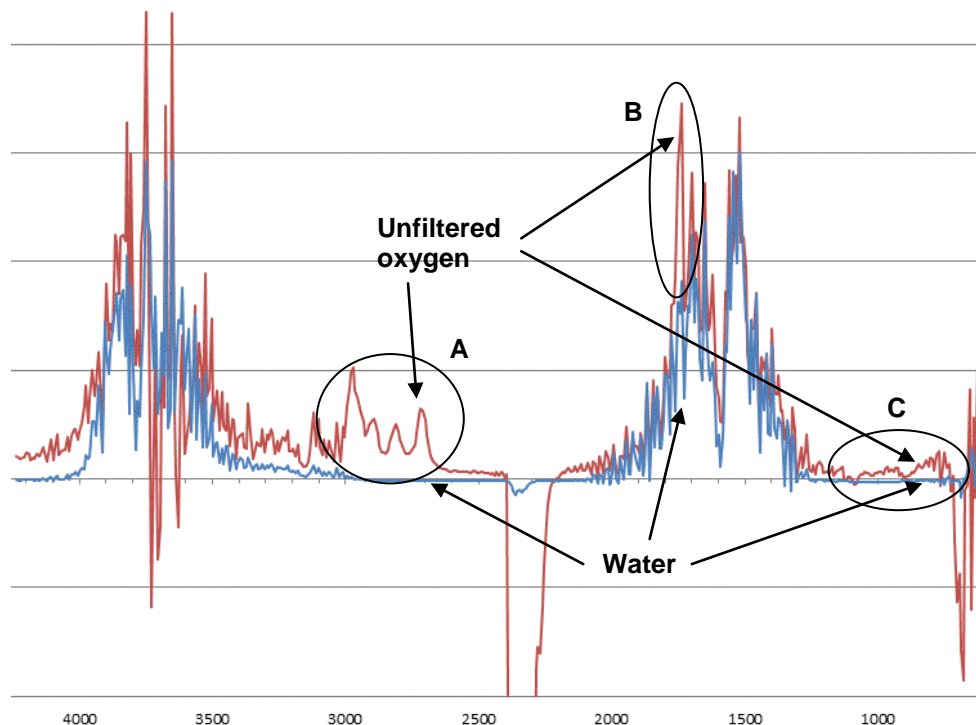

Figure 3: FTIR spectrum of unfiltered oxygen (upper) and water (lower). The oxygen spectrum differs from the water spectrum in areas A, B and C.

In Figure 4 the spectrums of the sample gas both with and without filtering are plotted. It is obvious that the peaks at wavenumbers in area A have disappeared after filtering of the oxygen gas. It could be argued that the spectrum has less absorption in areas B and C, but it is less evident than in A.
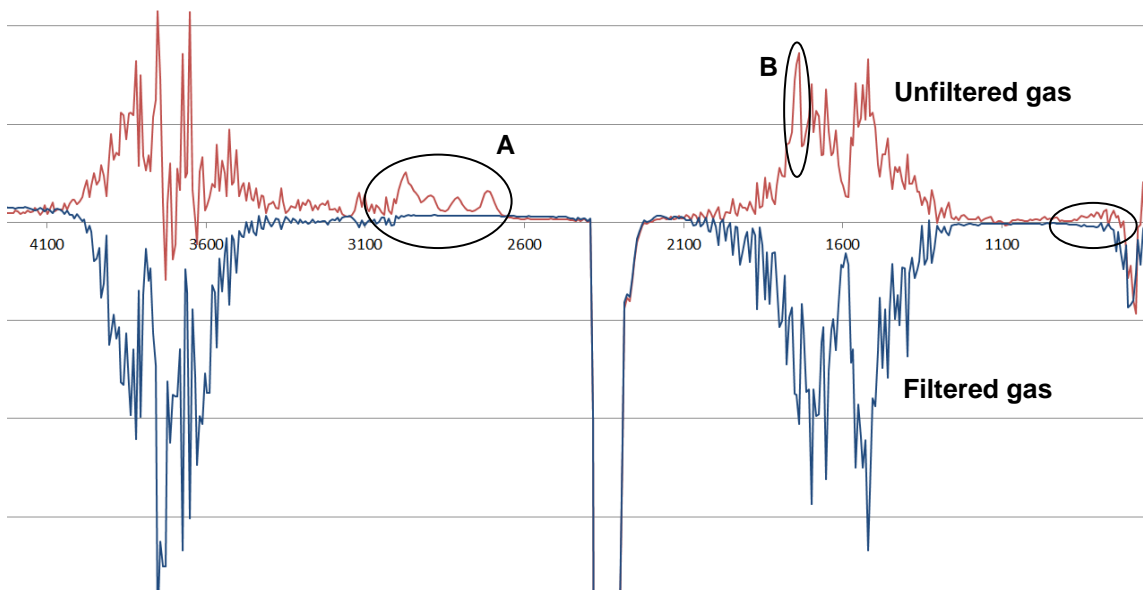

Figure 4: FTIR spectrum of filtered and unfiltered oxygen produced from hydrogen peroxide T49.5

Analysis with Dräger tubes

Dräger tubes [14] (shown left in Figure 5) are thin glass tubes filled with one or more active substances that changes colour when put in contact with certain gases. The gas for analysis is pumped through the tube by means of a dedicated pump (right in Figure 5) to assure a defined amount of sample gas. Analysis can be qualitative or quantitative and in some instance indicate more than one substance. Results from the analysis with and without the use of the developed filter are shown in Table I.

Figure 5. Dräger tubes (left) and pump (with courtesy of Dräger)

TABLE I. Analysis with Dräger tubes.

Chemical substance	Without filter	With filter	Comment
Formaldehyde	0.5 ppm	< 0.2 ppm	Could also be acetaldehyd
Acetaldehyde	1-10* ppm	< 1 ppm	*) Reading based on 100-1000 ppm scale
Amines	Negative	Negative	
Acetic acid	< 5 ppm	< 5 ppm	
Formic acid	< 1 ppm	< 1 ppm	
Hydrogen peroxide	< 0.1 ppm	< 0.1 ppm	

Analysis with Dräger tubes only indicates presence of acetaldehyde and possibly formaldehyde of the substances tested for. The meaning of "<" is "not detected" and the number following is the lowest number on the scale.

Conclusion from analysis

Results from FTIR analysis suggest that the contamination in the oxygen gas definitely has single C-H-bonds, which implies the presence of hydrocarbons. There is also indications of a C=O-bond matching an aldehyde or ketone. When comparing the boiling point of formaldehyde, acetaldehyde, propanal and butanal, the latter two can be ruled out as they would have been removed in the condensation trap. The analysis with Dräger tubes indicates that the gas contains acetaldehyde and possibly formaldehyde, two substances that also is hinted of in the literature.

It is quite evident that the filter system is removing undesirable components, as indicated both by the FTIR analysis and the Dräger tube analysis. Further, the odour of the produced oxygen had completely disappeared after passing the filter system.

24 hour test results

A 24 hour continuous test of the above described system was conducted in a pressure hull using bottled hydrogen and industrial hydrogen peroxide as reactants. The hull was fully immersed in an in-house water basin throughout the entire test to simulate the cooling conditions of surrounding sea water in an AUV application. The system showed stable and reliable performance throughout the test. Figure 2 shows the stack voltage and stack current. There is a small voltage decrease throughout the test. This trend was also observed during earlier tests in the development. It is most likely not related to impurities from the oxygen generator since the same behaviour also appeared when bottled oxygen of high purity was used. The voltage loss is largely recoverable, and the stack voltage is close to the last start value in the next run.
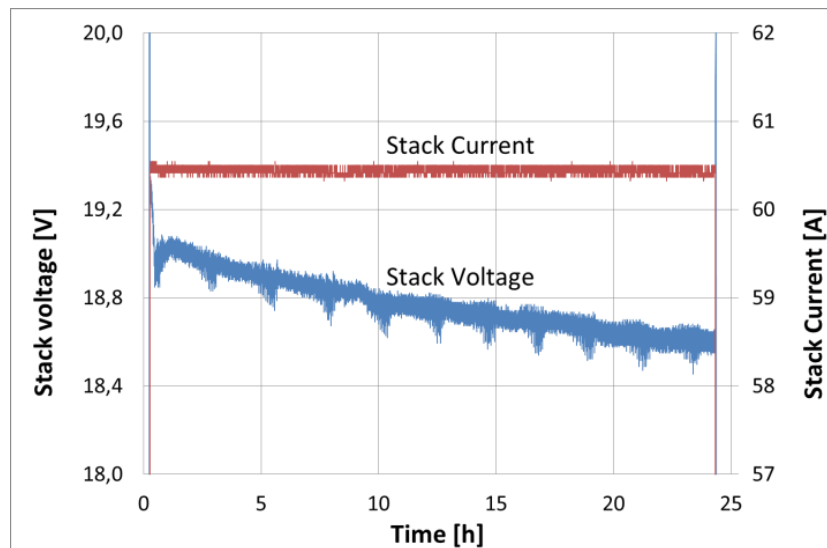
Figure 6. Stack voltage and current during the 24 hour test.

Figure 7 shows the pressure hull conditions during the same test. The air temperature, pressure and relative humidity reach levels within acceptable limits and these levels also stabilize shortly after start-up. This verifies that the cooling systems provide sufficient cooling of the atmosphere inside the hull, and that the water collection systems have sufficient capacity. It also verifies the functionality of the oxygen filters since there is evidently no significant build-up of impurities in the hull.
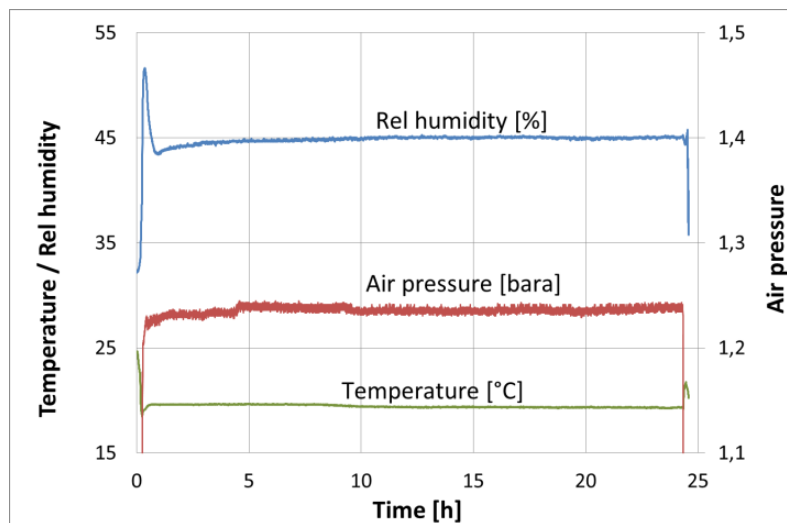

Figure 7. Pressure hull conditions during the 24 hour test.

Figure 8 shows that the hydrogen processing unit manages to keep the hydrogen concentration practically at zero throughout the test. The 0.04 % reading corresponds to the instrument offset. During start-up, however, the hydrogen level reaches 0.13 %. This is most probably due to hydrogen that has diffused through the membranes to the air channels during the initial start-up stages. When the air fan is started in the final start-up stages, this hydrogen exits into the hull with the outlet air causing the observed increase in hydrogen concentration. The observed concentration does however not pose any safety issue as it stays well below the lower explosion limit of 4 %. After the initial increase the

hydrogen concentration falls quickly towards zero, most likely as the hydrogen traces are drawn into the stack with the inlet air, where they react directly with oxygen on the cathode.
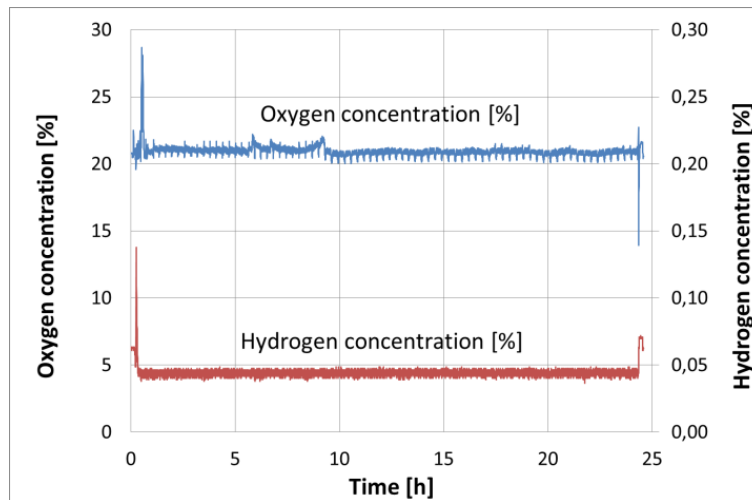

Figure 8. Oxygen and hydrogen concentrations in the pressure hull during the 24 hour test.

The oxygen concentration is maintained near 21 % throughout the test. The oxygen concentration sensor in the hull is sensitive to pressure changes, so the apparent concentration leap at start-up is a consequence of the pressure changes experienced when the air fan is started and does not stem from a real change in concentration. The smaller concentration fluctuations throughout the test are also due to pressure changes that disturb the concentration measurement and consequently also the oxygen supply control algorithm. Even though the fluctuations did not pose any problem to the overall system stability, this result shows that the oxygen concentration control algorithm has potential for improvement.

In summary, the 24 hour test verified the functionality of all subsystems, and that the developed fuel cell system can operate in a stable and reliable way in a sealed pressure hull under water.

Further work

Having verified the functionality and stability of the system, a natural next development step would be to install the system in an existing AUV and perform a sea trial. An important prerequisite is that a suitable hydrogen storage system is developed. The size and shape of the fuel cell system are designed to fit a commercial AUV from Kongsberg Maritime.

The sea trial would entail operating the fuel cell system in a diving AUV for several days. The AUV must operate autonomously at several hundred meters depth and include a selection of commercial sensors. Although there is a potential for further weight and volume reduction of the fuel cell system, the size and functionality is already at target for a demonstration, so major improvements are not necessary at the present stage. Further work at FFI should focus on developing a practical system for the hydrogen

source, either in the form of composite tanks or produced from metal or a liquid fuel in a reformer.

Conclusions

FFI has developed an air independent fuel cell system based on a water cooled PEM fuel cell stack from Ballard, bottled hydrogen and an in-house developed oxygen generator. The system was tested in a sealed pressure hull immersed in water, showing stable and reliable performance for 24 hours, operating automatically. The oxygen generator produced oxygen from hydrogen peroxide on demand. The gas analysis strongly indicated that the produced oxygen contained hydrocarbons, most likely acetaldehyde and possibly formaldehyde. A filter system was developed on basis of the analyses and was successful in removing undesirable components from the produced oxygen. The temperature and relative humidity of the air inside the pressure hull were kept well within acceptable boundaries during the test, and there was no build-up of hydrogen. The test verified the functionality and stability of the system.

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