Rechargeable Cryogenic Reactant Storage and Delivery System for Fuel Cell Powered Underwater Vehicles[1]

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Abstract

A cryogenic liquid oxygen storage system for providing oxygen to a fuel cell powered underwater vehicle has been proven feasible through a research program with the Office of Naval Research. A system has been designed that meets the Navy specifications of storing 50 kg and delivering 0.1 to 100 g/min of oxygen in an unmanned underwater vehicle. The total system mass has been shown to be practical for an underwater vehicle and the oxidizer mass ratios have been shown to be significantly greater than alternative oxygen storage techniques such as chemical or high pressure gas. Waste heat from the fuel cell has been shown to be a plentiful and effective heat source for vaporizing and pre-heating cryogenically stored liquid oxygen. The pre-hazard analysis has identified the potential hazards and countermeasures have been developed that will enable the liquid oxygen system to meet the high safety standards set forth by the Navy. A system design tool has been created that integrates a cryogenic reactant storage and delivery system with fuel cell design models using Visual Basic Application language. The system design tool is useful for conducting sensitivity analyses of key design parameters on overall system performance.

I. INTRODUCTION

The United States Navy is pursuing the use of underwater vehicles to serve as key elements in integrated operations of future surface ships and submarines, providing a range of support functions including autonomous surveillance, mine counter measures, and special forces transport. However, current power sources for these vehicles, primarily high energy batteries, do not meet the energy requirements for future missions, or they impose a tremendous logistics burden on the host vessel. Fuel cells offer a viable option for meeting mission energy requirements, and at the same time, they can reduce the host vessel logistics burden if the fuel and oxidizer can be generated onboard or stored in a high energy density format.

Fuel cells operating on hydrogen or more complex fuels (such as high energy density hydrocarbons) and oxygen are attractive as underwater power sources because they are efficient, quiet, compact, and easy to maintain. The total energy delivered by a fuel cell system is limited only by the amount of fuel and oxygen available to the fuel cell energy conversion stack. Unlike ground and air transportation fuel cell systems that only require onboard fuel, underwater vehicles must carry both the fuel and the oxygen source because the oxygen concentration in the ocean is insufficient to meet vehicle power requirements.

The generation, storage, and delivery of pure gaseous oxygen to the fuel cell stack within the closed environment of an underwater vehicle is therefore of primary concern to the Navy and poses a variety of challenges. First, the oxygen source must possess a high-oxygen content by both weight and volume to accommodate the weight and volume constraints of the vehicle design. Second, the oxygen source must be readily and rapidly replenished for maximum response time. Finally, the oxygen system must be capable of being operated safely and reliably in an autonomous mode from a variety of host vessels including surface ships and submarines.

The research presented here involves the merging of two broad technological fields, cryogenics and fuel cells. The results of which include the design of a rechargeable cryogenic liquid oxygen storage and delivery system for providing pure oxygen to a fuel cell powered underwater vehicle. The feasibility of the system and the benefits of using a liquid oxygen system over alternative storage techniques such as chemical or high-pressure gas are demonstrated. The hazards and effective countermeasures for oxygen and liquid oxygen systems are also presented. The broad impact of advanced cryogenic mass gauging and no-vent cryogenic reactant storage systems for hydrogen/oxygen fuel cells is also discussed.

II. UNMANNED UNDERWATER VEHICLE LOX SYSTEM DESIGN

A. Design Requirements

A cryogenic liquid oxygen storage system for providing oxygen to a fuel cell powered Unmanned Underwater Vehicle (UUV) has been designed. The system was designed based on the following Navy specifications for the UUV oxygen system.

- Store 50 kg of oxygen
- Provide oxygen flow rates of 0.1 to 100 gm/min to fuel cell (18 W to 10 kW of power)
- Configure system to fit inside a Mark 48 torpedo shell
- Maintain a high degree of safety
- Minimize impact to host vehicle operations
- Rapid turn around time

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B. LOX System Design

The Unmanned Underwater Vehicle LOX Storage and Delivery System flow schematic is presented in Figure 1. The LOX system shown is integrated with a Proton Exchange Membrane (PEM) fuel cell, which was chosen because it is a leading candidate as a power source for transportation vehicles. The major components designed and modeled include the LOX dewar, vacuum jacket heat exchanger, reactant pre-heater heat exchanger, PEM fuel cell, oxygen inlet conditioning system, oxygen control system with mass gauging and pressure control, and the fuel cell heat rejection water-cooling loop.

The UUV LOX system presented in Figure 1 has been designed to be modular. The LOX system module, which includes the dewar, oxygen control system (valves, piping, and instrumentation), and pre-heater, can be integrated into any type of vehicle or ground support system which requires a pure oxygen source or where air is not available. The LOX system module gives designers flexibility in the placement of the LOX system within the vehicle for optimization of the center of buoyancy for vehicle control purposes.

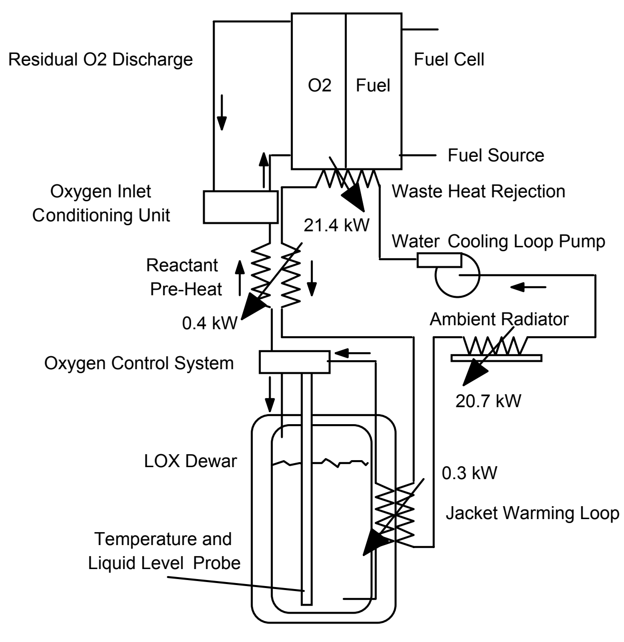

Figure 1: Unmanned Underwater Vehicle LOX Storage and Delivery System Schematic

The specific gravity of this module with 50 kg of LOX, 13 kg of structure, and a volume of 0.1871 m^3 is 0.34. The maximum expected operating pressure is 75 psia based on data that indicates PEM fuel cells operate more efficiently at 5 atmospheres of pressure (73 psia) than at 1 atmosphere of pressure. The current design is utilizing aluminum 6061-T6 for all cryogenic components. Figure 1 shows the water cooling loop energy balance for a PEM fuel cell producing 10 kW of electricity. The heat rejected from the fuel cell is 21.4 kW of which a total of 0.7 kW is required to vaporize and raise the temperature of the oxygen to the required PEM fuel cell inlet temperature.

The Oxygen Control System is designed to control gaseous oxygen flow to the fuel cell, liquid oxygen dewar pressure, and monitor liquid oxygen mass in the storage dewar. The Oxygen Control System utilizes the patented Cryo-Tracker™ Mass Gauging System (MGS) developed by Sierra Lobo, Inc. for measuring LOX mass during filling and operation. The MGS consists of the Cryo-Tracker™ temperature and liquid level sensing probe, electronics, and software. Figure 2 shows the probe installed from the lid of a cryogenic test tank at Sierra Lobo. The MGS integrates pressure, volume, liquid level, and temperature to accurately determine LOX mass. For more details on this system see References 1-4.

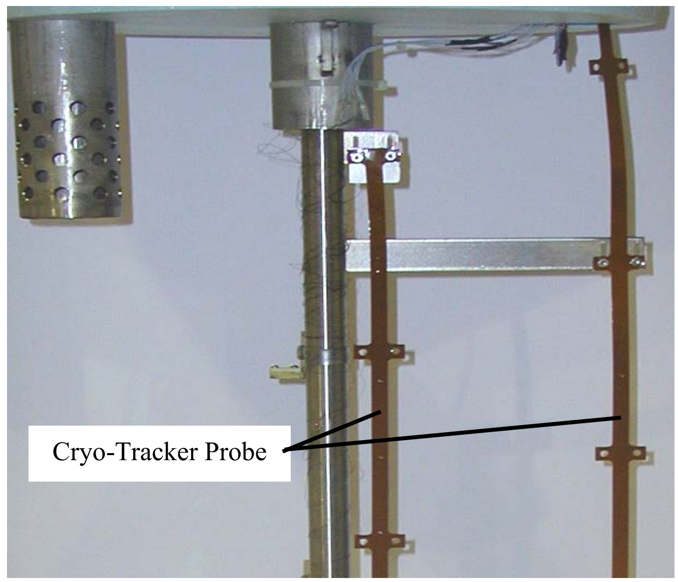

Figure 2: Sierra Lobo Cryo-Tracker™ Temperature and Liquid Level Sensing Probe Inside Cryogenic Tank

Figure 3 shows a layout of the vacuum jacked storage dewar and the reactant pre-heater heat exchanger in the Mark 48 torpedo. These two components are the most significant in terms of weight and volume that relate directly to the storage and delivery of liquid oxygen. The layout shows that there is sufficient room within the torpedo to arrange the components to accommodate valves and tubing. The components can be grouped together into a module that will give an UUV designer flexibility in sub-system integration and optimization.

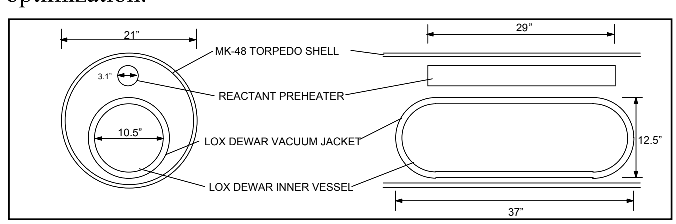

Figure 3: Unmanned Underwater Vehicle 50 kg Liquid Oxygen Storage and Delivery System Layout

C. System Operating Conditions

The liquid oxygen dewar on the UUV is pressurized by an autogenous pressurization system. The liquid is vaporized by absorbing heat from the vacuum jacket walls. The oxygen gas flow is controlled through the oxygen control system that will be programmed to control flow based on the current draw of the fuel cell. The oxygen enters the pre-heater where it is heated near the fuel cell operating temperature through heat exchange with the fuel cell cooling water. The oxygen inlet conditioning unit then mixes the residual oxygen discharge stream with pure oxygen and is injected into the fuel cell at the proper temperature, pressure, and humidity. The fuel cell water cooling loop provides heating to the pre-heater and vaporizer heat exchangers with the remaining waste heat being rejected to ambient or used by other systems on the vehicle.

D. System Design Tool

A design tool has been developed that integrates the Sierra Lobo Cryogenic Systems Design Tool with the PEM and Solid Oxide Fuel Cell (SOFC) fuel cell models developed by Case Western Reserve University. The design tool code was developed by Isotherm Technologies using Visual Basic Application (VBA) development language, which gives the code flexibility in terms of integrating with other applications such as EXCEL. The code development methodology is shown in Figure 4. The code has been constructed from a system designer's perspective with integrated models that provide unlimited flexibility. The System Design Tool allows for rapid changes in LOX system module designs and gives the designer additional flexibility in sizing dewars, heat exchangers, and eventually control systems for a particular application or vehicle. The System Design Tool calculates the performance for each of the key subsystems and feeds the results to the overall system model.

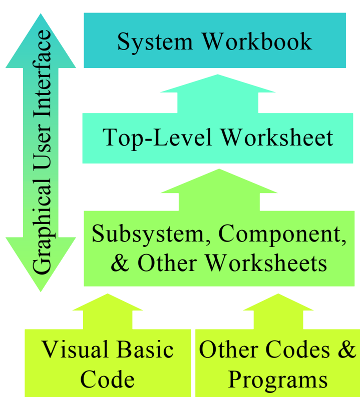

Figure 4: Fuel Cell and Cryogenic System Integrated Design Tool Methodology

E. PEM Fuel Cell Model

General fuel cell design models for PEM and SOFC were developed by CWRU for integration into the Cryogenic System Design Tool. Only the PEM fuel cell model will be discussed in this paper. The PEM fuel cell model develops a polarization (I-V) curve based on calculating typical PEM fuel cell losses from the open circuit potential per Equation 1. The polarization curve is shown in Figure 5. The curve gives cell voltage and power density as a function of current density.

$$V_{cell} = V_{oc} - iR - b\log\frac{i}{i_0} - b\log\frac{i_L}{i_L - 1} \qquad (1)$$

Where
- b = Tafel slope (V/decade)
- i = current density (A/cm^2)
- i_o = exchange current density (A/cm^2)
- i_L = limiting current density (A/cm^2)
- R = cell area resistance in (Ωcm^2)
- V_{cell} = cell potential voltage (V)
- V_{oc} = open circuit potential (V)

The anode and mass transfer losses in the model can be specified. The total cell area is scaled based on the I-V curve to yield 10 kW at 0.5V/cell. Reactant flows are calculated based on power output and hydrogen and oxygen utilization inputs. The heat duty is calculated assuming the fuel cell is isothermal and the outlet streams of hydrogen and oxygen are saturated. All product water is assumed to be removed in the oxygen stream. Pressure drop is currently being estimated.

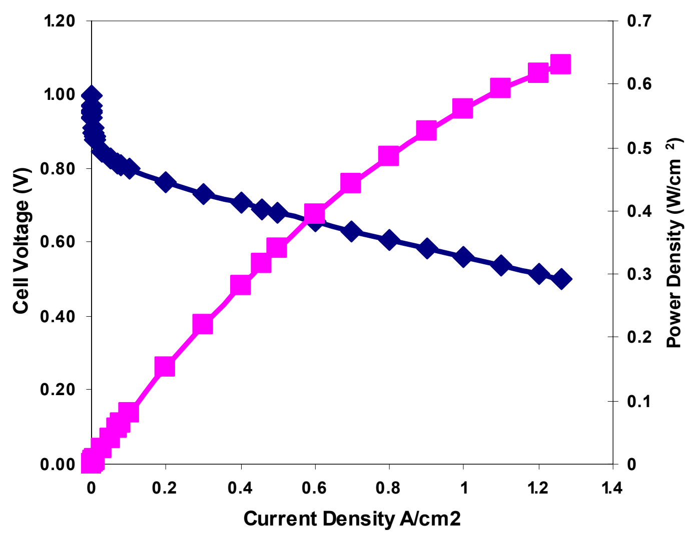

Figure 5: PEM Fuel Cell Polarization Curve Model

III. Oxygen Pre-Hazard Analysis

A pre-hazard analysis of the LOX storage system design configuration was conducted and presented in Reference 5. The pre-hazard analysis was conducted according to the guidelines given in Military Standard 882, System Safety Program Requirements (Reference 6). In addition, Hazards Analyses conducted by Sierra Lobo engineers on LOX systems related to testing and facility operations were reviewed and utilized. Military, NASA, and commercial standards for designing and operating liquid oxygen and cryogenic systems in general were reviewed and referenced as appropriate in the analysis (References 7-15).

The general approach used in conducting the pre-hazard analysis was as follows. The first step was to define the system. The next step involved dividing the system into subsystems and creating a hazard matrix. The causes and effects of each hazard were then identified. The severity and probability of each hazard-causing event was then identified and risk was calculated. Finally, countermeasures were recommended to reduce or eliminate the risk. The conclusion of this analysis showed that a cryogenic liquid oxygen storage system is safe when properly designed and operated.

The hazards matrix for the UUV as presented in the pre-hazard analysis is given in Table 1. This hazards matrix, which lists all UUV subsystems that may cause damage in the hazard groups as indicated with the (+). The dominant hazards are contamination, explosion, fire, and temperature extremes. Temperature extremes are the only hazard uniquely associated with a cryogenic system. All other dominant hazards apply to all oxygen generation and storage systems.

Table1
Unmanned Underwater Vehicle Hazard Matrix

	Oxygen System												Water System								
Hazard Group* / ***Subsystem*****	*Interface to Host*	*Storage Dewar*	*Cryo-Tracker*	*Heat Exchangers*	*Water Separator*	*Two-Phase Pump*	*Instrum. & Controls*	*Valves*	*Pipes*	*Electrical*	*Heater*	*Structural*	*Pump*	*Heat Exchangers*	*Heater*	*Instrum. & Controls*	*Valves*	*Pipes*	*Electrical*	*Ambient Radiator*	*Structural*
Collision	-	-	-	-	-	-	-	-	-	-	-	+	-	-	-	-	-	-	-	-	+
Mechanical Damage	-	-	-	-	-	-	-	-	-	-	-	+	-	-	-	-	-	-	-	-	+
Contamination	+	+	+	+	+	+	-	+	+	-	-	-	-	+	-	-	-	-	-	-	-
Corrosion	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Electrical Shock	+	-	-	-	-	-	+	-	-	+	-	-	-	-	-	+	-	-	+	-	-
Explosion	-	+	-	+	+	-	-	+	+	-	-	-	-	+	-	-	+	+	-	-	-
Fire	+	+	+	+	+	+	+	+	+	+	+	+	-	-	+	-	-	-	+	-	-
Loss of Habitable Atmosphere	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Pathological	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Psychological	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Radiation	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Temperature Extremes	+	+	-	+	-	+	-	+	+	-	+	+	+	+	+	-	-	-	-	+	-

*   Hazards groups defined by Reference 16.
** A subsystem failure or malfunction may cause damage in the hazard group(s) indicated.

IV. Benefits of UUV LOX Systems

A. Oxygen Storage

A comparison of several methods for storing 50 kg of oxygen is given in Table 2. These methods include chemical, high-pressure (HP) gaseous oxygen (GOX), normal boiling point (NBP) liquid oxygen, and triple point (TP) liquid oxygen. The storage system temperature, pressure, fluid density, tank mass, maximum tank length, and oxidizer mass ratio are given. The oxidizer mass ratio is the mass of oxygen divided by total oxidizer storage system weight which is oxidizer plus storage container mass. The chemical system assumes the release of oxygen from the burning of lithium perchlorate ($LiClO_4$) candles to produce lithium chloride (LiCl) and 2 moles of oxygen. Only the maximum theoretical oxidizer mass ratio based on the reaction equation is given in Table 2. The actual mass ratio will be lower. The high-pressure gaseous oxygen is stored in a lightweight, carbon-composite high-pressure cylinder. The cryogenic normal boiling point and triple point liquid oxygen is stored at low-pressure inside lightweight aluminum dewars at cryogenic temperatures. The dewar mass includes the inner vessel and the outer vacuum jacket vessel. The maximum outer diameter for the GOX and LOX systems was held constant at 0.27 m (0.88 ft).

Table 2
Oxygen Storage Systems Comparisons (50 kg of Oxygen)

		Chemical	HP GOX	NBP LOX	TP LOX
Tank Material	Units		CC	Aluminum	Aluminum
Temperature	K (F)		300 (80)	90 (-297)	54 (-362)
Pressure	KPa (psia)		34473 (5000)	101.3 (15)	101.3 (15)
Fluid Density	kg/m^3 (lbm/ft^3)		435 (27)	1142 (71.3)	1306 (81.5)
Mass	kg (lbm)		11.6 (25.6)	4.1 (9.1)	3.4 (7.6)
Maximum Length	m (ft)		2.2 (7.07)	0.497 (3.08)	0.475 (2.76)
Oxidizer Mass Ratio		0.60 max	0.81	0.92	0.94

The comparison presented in Table 2 clearly shows the advantages of the cryogenic LOX storage system over the chemical and high-pressure oxygen system. The benefits include:

- Tank mass reduction of 64 to 70% over high pressure GOX storage
- Tank length and volume reduction of 56 to 61% over high pressure GOX storage
- Oxidizer mass ratio increase of 14% over GOX storage and 56% over chemical

B. Fuel Cell Systems

Table 3 gives the specific energy of twelve different fuel cell systems that use different combinations of fuel and oxidizer (Reference 17). The fuel cell types studied by the Office of Naval Research are the Proton Exchange Membrane (PEM), and Solid Oxide Fuel Cell (SOFC). The fuel types included logistic or military grade diesel fuel commonly used in the fleet, synthetic diesel, and methanol through the Direct Methanol Fuel Cell (DMFC), and the Direct ElectroChemical Oxidation (DECO) fuel cell. Several targets are set for DECO fuel cells including, Air Independent Propulsion (AIP) and Air Augmented Options. The oxidizer types investigated included chemical oxygen, hydrogen peroxide, and liquid oxygen. The data shows that LOX systems provide significantly higher specific energy than comparable fuel cell types that use other oxygen sources such as chemical and hydrogen peroxide.

Table 3
Specific Energies of Different Fuel Cell Types

System No.	Fuel Cell Type	Oxidizer	Specific Energy (Whr/kg)
1	PEM w/ Logistic	Chemical O2	367
2	PEM w/ Logistic	Chemical O2	284
3	PEM w/ Logistic	LOX	544
4	PEM w/ Syn-Diesel	LOX	602
5	PEM w/ Syn-Diesel	60% H2O2	294
6	PEM DMFC	LOX	575
7	SOFC w/ Logistics	LOX	713
8	SOFC DECO#1 (Near-Term)	LOX	643
9	SOFC DECO#2 (Long-Term)	LOX	887
10	SOFC DECO#3 (2x Energy)	LOX	1013
11	SOFC DECO#2 (AIP-Air Option (50:50)	LOX	1172
12	SOFC DECO#1 AIP-Air Option (50:50)	LOX	816

The cumulative weight of each of the fuel cell systems given in Table 3 are shown in Figure 5. For each fuel cell system the mass is given for the fuel cell, fuel, reformer and pump, oxygen system, CO_2 system, and other auxiliaries. On average the oxygen system is over 50% of the total propulsion system weight. Reducing oxygen system weight therefore has the greatest impact on reducing the overall weight of the system. The data shows that use of a LOX system, rather than a chemical oxygen system will decrease the overall system weight by 48% for a given type of fuel cell propulsion system. (See System 2 versus System 3.)

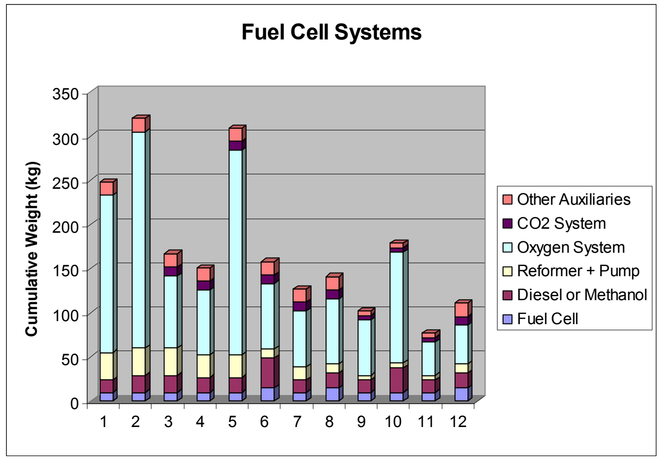

Figure 6: UUV Propulsion System Weights for a 100kWh @ 4 kW Fuel Cell

V. Cryogenic Fluid Management Options

A. Requirements

Several options are presented with regard to implementing a Cryogenic Fluid Management (CFM) system for loading an Unmanned Underwater Vehicle with cryogenic reactants from a host vehicle. These options are derived based on general requirements of the host vehicle to support an Unmanned Underwater Vehicle. The requirements taken into consideration include: maintaining existing safety standards, minimizing the impact to crew responsibilities (high degree of autonomy), rapid turn around times, and minimized footprints. The main assumptions in this research are that the host vehicle is a submarine and that the submarine maintains an on-board high-pressure water electrolyzer that generates high-pressure gaseous oxygen for breathing air and gaseous hydrogen as a by-product.

B. CFM Option Descriptions

Three options for Cryogenic Fluid Management are presented in Figure 7. The first option is the direct liquefaction of gaseous oxygen. First, the host vehicle high-pressure gaseous oxygen is regulated down to a lower pressure. Then a one stage commercially available cryocooler coupled to a heat exchanger can be used to liquefy the GOX directly into the host vehicle cryogenic LOX storage system dewar. This is the simplest LOX loading system. The heavy (~120 kg) cryocooler compressor can be located on the host

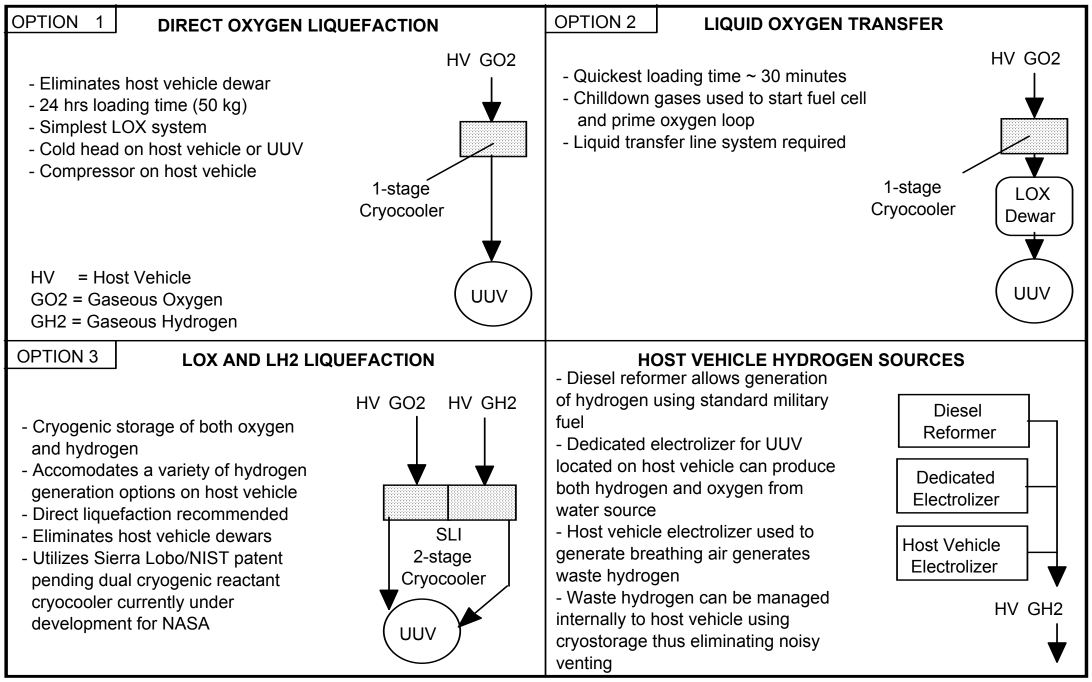

Figure 7: Host Vehicle Cryogenic UUV Systems Support Options including Oxygen and Hydrogen

vehicle and the relatively light (17 kg) cryocooler cold head and heat exchanger can be positioned on either the host vehicle or the UUV. A host vehicle LOX dewar is not required. The loading time for 50 kg of LOX is approximately 24 hours based on a single cryocooler of reasonable size. Multiple cryocoolers can be utilized in parallel to decrease loading time as required.

The second option is a liquid oxygen transfer from a storage dewar on the host vehicle into the UUV LOX storage dewar. This option provides the quickest LOX loading time of less than 30 minutes. The system chilldown gases generated can be used to start the fuel cell and prime the oxygen loop. A liquid transfer line is required for this system.

C. Hydrogen CFM

The third option is the liquefaction of both oxygen and hydrogen using the new and unique pulse tube cryocooler under development by Sierra Lobo, Inc. for the National Aeronautics and Space Administration (NASA). The new cryocooler is shown in Figure 8. The cryocooler is a patent pending dual cryogenic fluid densification system, which can also be used for liquefaction. The cryocooler has two stages as indicated in Figure 8. The first stage is designed to densify or liquefy oxygen and the second stage is designed to densify or liquefy hydrogen. Both stages can operate simultaneously down to the triple point temperatures of their respective fluids. This option accommodates a variety of hydrogen generation options on the host vehicle and eliminates host vehicle storage dewars.

Liquid hydrogen storage is investigated for a number of reasons. First, the UUV host vehicle has several options for generating hydrogen. Second, the PEM fuel cell requires hydrogen for operation. Third, the hydrogen is pure and does not contain contaminates that can degrade the fuel cell performance with time. Finally, the use of hydrogen eliminates the need for a reformer and additional heat exchangers on board the UUV for hydrocarbon fuels.

The host vehicle has several options for generating hydrogen. The three options for generating hydrogen that can be liquefied on-board the UUV are summarized in Figure 7. The hydrogen sources are diesel fuel reformer, a small dedicated water electrolyzer for the UUV, and the larger host vehicle water electrolyzer. The diesel fuel reformer allows the generation of hydrogen using a standard military fuel. The small dedicated electrolyzer can split water into hydrogen and oxygen locally near the UUV. The host vehicle electrolyzer, used to generate breathing oxygen, generates waste hydrogen which is normally vented overboard. A portion or all of this hydrogen can be liquefied and stored on the host vehicle while the remaining is condensed into the UUV. Noisy venting of hydrogen could be eliminated at specific times during a critical mission.

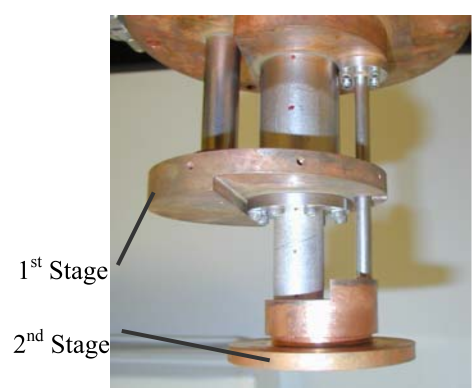

Figure 8: Sierra Lobo Two-Stage Pulse Tube Cryocooler

VI. Conclusions

In general, the research has resulted in the successful integration of technology from two broad fields: cryogenics and fuel cells. The integrated system design tool that has been developed can be used to design cryogenic reactant storage and delivery systems for different types of cryogenic reactants, fuel cell types, and system operating conditions. Cryogenic fluid management techniques have been developed that utilize advanced cryogenic liquid mass gauging and cryocooler technologies for loading cryogenic reactants and maintaining them in a safe no-vent condition.

More specifically, a cryogenic liquid oxygen storage system for providing oxygen to a fuel cell powered underwater vehicle has been proven feasible. A system has been designed that meets the Navy specifications of storing 50 kg and delivering 0.1 to 100 g/min of oxygen. The total system mass has been shown to be practical for an underwater vehicle and the oxidizer mass ratios have been shown to be significantly greater than alternative oxygen storage techniques such as chemical or high pressure gas. Waste heat from the fuel cell has been shown to be a plentiful and effective heat source for vaporizing and pre-heating cryogenically stored liquid oxygen. The pre-hazard analysis has identified the potential hazards and has developed countermeasures that will enable the liquid oxygen system to meet the high safety standards set forth by the Navy.

VII. Acknowledgements

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