TECHNICAL ISSUES AND OPPORTUNITIES FOR FUEL CELL DEVELOPMENT FOR AUTONOMOUS UNDERWATER VEHICLES

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***Abstract*- The efficiency and quietness of fuel cells make them attractive power sources for the autonomous underwater vehicles of the future. However, several technical issues must be addressed before fuel cells can surpass the performance characteristics of batteries, including efficiency, reliability, durability, standby operation and storage, changes to orientation, and high shock loads. Improvements to the storage of the fuel (hydrogen or hydrogen sources) and oxidizer (oxygen) make the biggest impact on the size, weight, and utilization of fuel cell systems. Proton-exchange-membrane fuel cells (PEMFCs) are the most attractive fuel cell system and already have been successfully demonstrated for use in Autonomous Underwater Vehicles (AUVs). AUVs of the future may utilize direct-methanol fuel cells (DMFCs) or solid-oxide fuel cells (SOFCs) which can use liquid methanol or diesel fuel instead of hydrogen.**

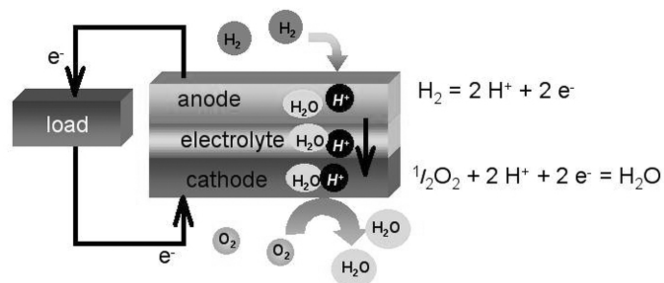

Fig. 1. Schematic diagram of a proton exchange membrane fuel cell. Hydrogen is electrocatalytically converted to protons at the anode. The protons conduct through the hydrated electrolyte to the cathode where they electrocatalytically combine with oxygen to form water. The electrons from the electrocatalytic reaction pass through an external load. Cell potentials range from 0.5 to 0.8 V.

I. INTRODUCTION

Fuel cells are recognized as efficient, silent, clean energy conversion systems [1,2]. A schematic of a fuel cell is shown in Fig. 1. Electricity is produced when a fuel (e.g. hydrogen) and an oxidizer (e.g., oxygen) react electrochemically to produce water and electrons. Because fuel cells produce electricity via electrochemistry, the efficiency of the fuel cells is higher than that of mechanical systems. The efficiency of air-breathing fuel cells with hydrocarbon fuels range from 30 to 55%, depending on the type of fuel cell (Table I) and is a function of the energy created from the fuel/oxidizer reaction minus resistive losses within the electrochemical cells, thermal losses, and the drain of auxiliary components. The energy needed to extract hydrogen from a fuel or water also taxes the total system efficiency. Fuel cells have higher efficiencies (~70%) when operated on hydrogen and oxygen.

The high fuel-conversion efficiency of fuel cells leads to high specific energies and energy densities, making them attractive power systems for AUVs [3,4]; however numerous technical challenges must be solved before they will provide a clear benefit over batteries. A fuel cell operating on stored hydrogen and air can have an energy density in excess of 1000 Wh/kg, which far exceeds that of silver-zinc or lead-acid batteries (150 and 43 Wh/kg, respectively). For undersea applications, the fuel cell oxygen obviously must be carried. The additional weight and space needed to store the oxygen lowers the energy density of a fuel cell with stored fuel and oxidizer to 200 – 400 Wh/kg.

This manuscript describes technical issues associated with hydrogen and oxygen storage, plus different types of fuel cells, and opportunities for their use in AUVs. Semi-fuel cells, which utilize aluminum or another metal as the fuel, are beyond the scope of this paper. More information can be found elsewhere [3-6].

TABLE I
OPERATING TEMPERATURE AND EFFICIENCY OF DIFFERENT FUEL CELLS

Fuel cell type	Operating temp (°C)	Efficiency Air/CH_4	Efficiency O_2/H_2
Proton exchange membrane	70-90	30-35%	66-73%
Phosphoric acid	190-215	35-40%	--
Molten carbonate	600-650	45-50%	--
Solid oxide	700 - 1000	50-55%	70%

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II. Types of Fuel Cells

There are six common types of fuel cells: alkaline, proton exchange åmembrane, direct methanol, phosphoric acid, molten carbonate, and solid oxide [1]. The fuel cells differ predominantly in their electrolytes, which in turn drive the optimum temperature for operation and choice of catalysts (Table I). The most favorable fuel cells for AUVs are proton exchange membrane, direct methanol, and solid oxide fuel cells. Alkaline fuel cells operate at low temperatures, like PEMFCs, but are confined to working on ultra-pure hydrogen and oxygen, so they are not developed for commercial use. Phosphoric acid fuel cells (PAFCs) and molten carbonate fuel cells (MCFCs) are less compact than the other fuel cells.

Proton exchange membrane fuel cells (PEMFCs) are currently the subject of intense research and development for use in automobiles [2] and portable power. These fuel cells operate near 80 °C, and platinum must be used for both the fuel and oxidizer electrodes to efficiently catalyze the oxidation of hydrogen and reduction of oxygen, respectively. The electrolyte separating the electrodes is a proton (H^+) conducting polymeric membrane, such as Nafion®, a perfluorosulfonic membrane that is mechanically strong and chemically stable. Because of their low-temperature operation, water management is a critical concern in the design of PEMFC power systems.

The attraction of PEMFC systems is their high specific energy. A disadvantage of PEMFCs is that they require a pure source of hydrogen fuel, because impurities (e.g., hydrogen sulfide and carbon monoxide) left from reforming a hydrocarbon hydrogen source poison the platinum catalysts, and render the fuel cell inactive. Fortunately, the management and cost of a high-quality source of hydrogen is not a critical problem for Naval systems.

A derivative of PEMFCs is direct methanol fuel cells (DMFCs) [7]. With the use of platinum-ruthenium catalysts at the anode, methanol diluted in water can be used as the fuel source in a polymer fuel cell instead of hydrogen. The use of methanol eliminates some of the issues associated with hydrogen storage. The critical deficiency to this technology is the low energy due to non-optimized reaction of the methanol and the leakage of methanol from the fuel to oxidizer compartments. DMFCs are most efficient for low-power usage (<500W).

Solid oxide fuel cells (SOFCs) offer the highest efficiencies due to their high-temperature operation (600 – 1000 °C). These all-ceramic fuel cells are composed typically of a strontium-doped lanthanum-manganese-oxide cathode, a yttria-stabilized zirconia (YSZ) electrolyte, and a nickel-YSZ cermet anode. The YSZ electrolyte is an oxygen-ion (O^{2-}) conductor. SOFCs can be integrated with logistic fuel reformers because, at their high operating temperature, they oxidize the carbon monoxide emitted by the reformers. They are also tolerant to low levels (<50 ppm) of hydrogen sulfide. Disadvantages of using SOFCs for AUVs are their thermal signature and their lack of ruggedness. Lower temperature operation at 400 to 600 °C may eventually be possible with the development of new materials.

As methanol can be directly converted in PEMFCs, it may soon be possible to directly utilize logistics fuels in SOFCs. Recent research has shown that when the Ni-YSZ cermet anodes are replaced with Cu-YSZ-CeO_2, diesel fuels can undergo direct electrochemical oxidation at the anode [8], eliminating the need for a reformer and water to externally convert the hydrocarbons to hydrogen. The high sulfur contents of standard diesel fuels (5000 to 20,000 ppm) will poison these fuel cells, but it may be possible to use low-sulfur diesels or sulfur-free synthetic diesels in such SOFCs.

IV. Technical Issues for Fuel Cells for AUVs

A. System and Balance of Plant

To replace the batteries currently used in AUVs, fuel cells must meet or beat criteria for high safety, efficiency, reliability, and durability, plus the fuel cell must be able to maintain performance despite standby operation and storage, changes to orientation, and high shock loads. In addition, fuel cells for AUVs must be able to function in confined spaces, and thus there must be a means for handling any leaking hydrogen and oxygen. Neutral buoyancy must be maintained, so ballast is added to offset the storage of light gases, and the water generated from the electrochemical reaction is stored. There can be no change to the weight distribution in the AUV as the fuel and oxidizer are consumed and water is created.

B. Hydrogen and Oxygen Storage and Management

The storage of oxygen and hydrogen is a critical issue for AUVs. The weight and size of storage tanks significantly impacts the specific energy and energy density of the fuel cell system. Safety relief valves are required and must exhaust into the outside water. Therefore, the storage tanks must be able to withstand a pressure greater than the external pressure at the submerged depth. The system design must also include a strategy to recombine any leaking gases.

1) *Hydrogen:* There are currently significant research efforts to create effective hydrogen storage capabilities for use on PEMFC-powered automobiles. Although hydrogen is very light, its volumetric density is poor when stored as a gas. When hydrogen is stored in high-pressure tanks, the weight percent of hydrogen in the system is low, typically 2 to 4%. With improvements in the tank materials, significant improvements have been recently gained, and there are recent

Contents

reports of composite tanks that can store up to 11% hydrogen at 5000 psi. Such high-pressure tanks require liners to prevent gas leakage. Hydrogen-storage tanks can be recharged numerous times (>100) before they become fatigued by hydrogen embrittlement.

Storing hydrogen in a metal hydride is attractive for AUVs because it solves any problems associated with high-pressure gases and ballast. Common hydrogen storage alloys include $LaNi_5$, FeTi, Mg_2Ni and ZrV_2. The amount of hydrogen that can be stored in the metals ranges from about 1 to 8 %. The metal hydrides must also be stored in reliable low-leakage packaging. Heat is often required to liberate the hydrogen from the metal. While metal hydride alloys are reversible hydrogen storage media, the alloys can lose their storage efficiency as they are recharged over multiple cycles. Carbon nanotubes are also under intense investigation as hydrogen-storage materials.

Chemical sources of hydrogen are another viable option for fuel-cell-powered AUVs. Ammonia (NH_3) can be catalytically decomposed at elevated temperatures to provide a clean source hydrogen. Sodium borohydride ($NaBH_4$) and various aluminum hydrides (e.g., $LiAlH_4$) are other good hydrogen sources. Such chemical hydrogen sources must be mechanically replaced for refueling.

Storage of hydrogen as a cryogenic liquid is also an option for AUVs. Under cryogenic conditions, hydrogen is in a supercritical phase so its weight distribution in the storage tank remains uniform during AUV maneuvers.

2) *Oxygen*: Oxygen storage is an issue specific to fuel cells for undersea and space applications. The oxygen content of water (150 µmole O_2/L at depths of 600 m) is too low to make oxygen harvesting through a gill system practical for high-power fuel cell operation, so oxygen must be carried with the undersea vehicle.

Chemical storage sources of oxygen include hydrogen peroxide, $LiClO_4$, $NaClO_3$ (oxygen candles), other oxyhalides, and peroxides/superoxides. While such chemical oxygen sources provide excellent volumetric storage of oxygen, particularly $LiClO_4$, they suffer a weight penalty from the presence of non-oxygen atoms and unreleased oxygen. They also require mechanical replacement during fuel cell refueling and thus mandate storage of these highly oxidizing chemicals in on the host platform. In addition, thermal or catalytic processes are needed to release the oxygen from these compounds, thus adding complexity to the overall fuel cell system. In fact, estimates of various component weights in an AUV PEMFC system indicate that chemical oxygen sources are likely to constitute over 65% of the total system weight.

The use of pure oxygen in AUV fuel cell systems offers numerous advantages including continual oxidant replacement upon refueling, a reduction in the overall system weight, and a simplified oxygen delivery system. While high-pressure oxygen is a possible storage method, the use of cryogenic liquid oxygen (LOX) is the optimal approach for storage in a confined space. A drawback of using LOX is that stringent conditions must be met for its safe handling and storage. The latter can be mitigated by producing LOX "on demand" from a low or high-pressure sources of oxygen gas on the host platform.

IV. Development Programs for Fuel Cells for Undersea Vehicles

The Defense Advanced Research Projects Agency (DARPA) sponsored International Fuel Cells (IFC) to develop a PEMFC to power a 44-inch unmanned undersea vehicle [3,4,9]. The 15-kW power plant comprised four fuel cell stacks and an accessory section. To meet the safety and performance criteria for undersea military missions, IFC utilized a simple system concept which required no circulation of gases for thermal and water management. In 1994, the UUV fuel-cell system was operated successfully for over 500 hrs, but was never tested at sea due to programmatic (cost and schedule) considerations.

Concomitant with the IFC project, DARPA also sponsored Loral Defense Systems to develop an aluminum semi-fuel cell by Loral [3,4,6], but the discussion of this program is beyond the scope of this manuscript.

PEMFCs are integral to the new power systems for the 212-class submarines of Howaltsverke-Duetsche Werke (HDW) of Kiel, Germany [10]. The nine Siemens PEMFCs provide 250 to 400 kW of power for silent, air-independent propulsion (AIP). The fuel cell cannot be used as the sole power source, because it lacks the power for high-speed operations, so lead-acid batteries are also used in parallel with the fuel cells to supply high power. A conventional diesel generator is also on board. The AIP allows the ship to stay submerged for more than a month and travel up to 3000 miles without refueling. To accommodate the stored oxygen and hydrogen needed for air-independent fuel cell operation, the hull section of the submarine must be extended 30 feet. The hydrogen is stored in metal hydrides, and liquid oxygen is stored in the double hull. Both Germany and Italy have commissioned the purchase of these 212-class submarines. Sea testing is underway and commissioning is expected for 2004.

The US Office of Naval Research and the Defense Science and Technology Laboratory (Dstl) in the United Kingdom have entered into a joint program to develop PEMFC-based power systems for AIP of AUVs. To meet the high energy density goals of the program, an alkaline solution of sodium

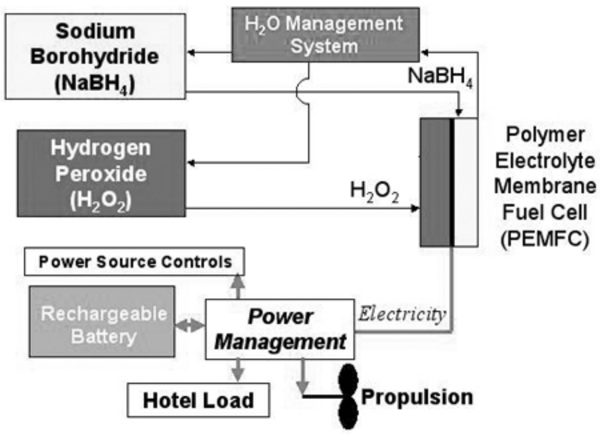

Fig. 2 Schematic diagram of the fuel cell system currently under development by the US Office of Naval Research and the UK Defense Science and Technology Laboratory (Dstl). Sodium borohydride serves as the fuel and hydrogen peroxide is used as the fuel in a PEMFC.

borohydride ($NaBH_4$) is being examined as the fuel while LOX or liquid hydrogen peroxide (H_2O_2) are proposed as the oxidizer. Rechargeable batteries are likely to be included to meet high power demands and provide independent startup capabilities. A schematic diagram of such a conceptual system is shown in Fig. 2.

ONR and DARPA are also supporting the development of direct diesel oxidation at SOFC anodes, and the success of that technology could ultimately lead to the implementation of logistics-fueled SOFCs as power systems for AUVs.

V. Summary

AUVs of the future may be powered by energy-dense fuel cells, such as PEMFCs, DMFCs, or SOFCs. PEMFC technology is more mature than the others. A PEMFC system operates at low temperatures and is likely to be supported by a hydrogen storage system. A DMFC operates on a convenient, but low energy density liquid fuel. SOFC systems operate at high temperatures and therefore may be operated from logistic fuels that are either externally reformed or directly oxidized at the anode. The implementation of fuel cells in AUVs requires consideration of specific systems issues, plus storage of the fuel and oxidizer. The fuel cells can be expected to have higher energy density and specific energy than any secondary battery.

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