NaBH$_4$/H$_2$O$_2$ fuel cells for air independent power systems

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ABSTRACT

The performance and characteristics of direct sodium-borohydride/hydrogen-peroxide (NaBH$_4$/H$_2$O$_2$) fuel cells are studied in the context of potential applications for air independent propulsion for outer space and underwater. Due to the existence of ocean (sea) water as a natural heat sink, this new fuel cell technology is best suited for underwater propulsion/power systems for small scale high performance marine vehicles. The characteristics of such a power system are compared to other options, specifically for the underwater scenario. The potential of this fuel cell is demonstrated in laboratory experiments. Power density over 1.5 W cm^{-2}, at 65 °C and ambient pressure, have been achieved with the help of some unique treatments of the fuel cell. One such treatment is an in-situ electroplating technique, which results in electrodes with power density 20–40% higher, than that of the electrodes produced by the ordinary ex-situ electroplating method. This unique process also makes repair or reconditioning of the fuel cell possible and convenient.

1. Introduction

Air-independent propulsion (AIP) applications for space or underwater environment were among the motive forces for the initial development of fuel cell (FC) technology starting in the 1950s. The fuel cells for NASA's Gemini, Apollo and Space Shuttle programs [1], and the recent fuel cell-based AIP systems for the Howaldtswerke-Deutsche Werft (HDW) Type-212/214 submarines [2] are all witness to such a retrospect on the history of FC technology development. In most cases, cryogenic liquid oxygen is carried as the oxidizer, which invariably evaporates over a few weeks, limiting the mission time. On the hydrogen side, the space based FC often uses cryogenic hydrogen, in order to minimize the mass of FC systems. This approach, however, leads to even more limited mission time due to the exceptionally high boiling-off rate of liquid hydrogen, even for a very well designed and engineered Dewar system. To address such an issue, hydrogen was carried in metal-hydride cylinders in the Type-212/214 AIP systems instead [2]. While compact volume-wise, the heavy weight of the metal-hydride system results in significant loss of the overall energy density.

Fuel cells based on NaBH$_4$/H$_2$O$_2$ have generated substantial interests recently [3–8], and the initial results are very promising. The general feasibility of a borohydride/peroxide electrochemical cell has thus been demonstrated. For space or underwater power

applications where air independence is a must, H$_2$O$_2$ based fuel cells offer an ideal solution.

Fuel cells typically have an efficiency of 50% or lower at the maximal power, which is low compared to that of a battery. For example, a 10-kW FC power system can generate on the order of 10 kW of waste heat during its operation. For outer space, to reject this amount of heat could pose substantial engineering issues in such a nearly vacuumed environment. For underwater applications, however, heat sink is not a problem at all with the presence of the ocean water. Furthermore, water itself can possibly work as a reactant, typically as an oxidant, saving the needs to carry oxidizer onboard, for some really demanding power systems. An electrochemical engine then can take in water, using it in the electrochemical reaction, and then generates power. This is much like an air breathing engine's taking-in the air, mixing it with a fuel, which is then combusted to do the mechanical work. Such a scheme would greatly increase the specific impulse, translating into longer range and operational duration.

The adoption of peroxide might still face a psychological barrier when used in manned underwater vehicles, due to safety concerns associated with high test peroxide (HTP). However, all energetic systems are inherently dangerous. For example, high-pressure or cryogenic oxygen, when not properly handled, could also lead to disastrous results, manifested by the M-256 (a submarine of the Soviet era) and the Challenger (the NASA Space Shuttle) accidents. The safety concerns, however, are less pressing for unmanned underwater vehicles (UUVs). Therefore, the adoption of NaBH$_4$/H$_2$O$_2$ fuel cell is likely to start with UUVs, especially

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the smaller ones where the cost of borohydrides will be of less significance. We focus our attention on small UUVs in this paper.

2. Unique requirements for underwater power systems

The requirements on any mobile power system are in general light weight, high energy density, and high power density. Besides these, the underwater environment places a few additional demands to maximize the platform's potential.

2.1. Neutral buoyancy

UUVs typically need to dive and surface at will with minimal amount of dynamic forces. This requires that the vessel is nearly neutrally buoyant. The fuel and oxidizer are therefore preferably neutrally buoyant, which means that they have a specific gravity close to $1\,\mathrm{g\,cm^{-3}}$, which is that of water. In this regard, the $NaBH_4/H_2O_2$ combination is a very good option, which averages to $1.2\,\mathrm{g\,cm^{-3}}$. On the other hand, for fuel cell systems using stored molecular hydrogen, this requirement poses a problem. High pressure storage, even in the 1000 bar range, still faces the problem of bulkiness, meaning it is difficult to dive. On the other hand, a metal hydride-based H_2 storage will be just too heavy.

2.2. Depth independent power output

The depth independence of power output is easy to understand from an operational perspective. This property is associated with whether the power conversion cycle is open or closed. The nature of the cycle really depends on whether the underlying chemical reaction is volume increasing or not. If the volume of the reaction products increases significantly compared to that of reactants, i.e., more gas is generated, the power conversion cycle is likely to be open. As an example, if the fuel is a hydrocarbon or an alcohol, and the oxidizer is rich in oxygen, the reaction products are likely to include carbon dioxide. Although CO_2 could be absorbed into sea water, given a large enough disposer, the increased oceanic backpressure to the CO_2 generation reaction will significantly shift the chemical reaction backwards. This reduces the power output of the energy conversion unit, be it a heat engine or a fuel cell. For $NaBH_4/H_2O_2$ no such a problem exists because the reaction is nearly constant in volume.

2.3. Silence

The sensor array that is almost ubiquitously carried by UUVs requires silence from the power system. Fuel cell is advantageous over a heat engine in this regard, due to its inherent quietness. The fuel combination also plays a role, nevertheless. A fuel cell cycle which generates a lot of gas is no longer silent when exhausting gas bubbles into the ocean water. With CO_2 generated, for example, the power conversion is not a true closed cycle. The release of gas off-board invariably generates loud noises.

The three requirements unique to underwater power systems for UUVs pose strong constraints on the fuel/oxidizer combination and the energy conversion process.

3. Fuel/oxidizer combination for underwater powers

We consider a number of different fuel/oxidizer combinations that are conceivable for underwater propulsion. The options listed in Table 1 are those considered more or less environmental benign or those that have been in service for quite sometime. Notably

Table 1
Specific thermal energy release of various fuel-oxidizer combinations, calculated from standard thermodynamic enthalpy [9].

Fuel/oxidant	Reaction	Energy density $(MJ\,kg^{-1})$
H_2/H_2O_2	$H_2 + H_2O_2 = 2H_2O$	10.65
MgH_2/H_2O_2	$MgH_2 + 2H_2O_2 = Mg(OH)_2 + 2H_2O$	11.07
$NaBH_4/H_2O_2$	$NaBH_4 + 4H_2O_2 = NaOH + B(OH)_3 + 4H_2O$	10.20
$LiBH_4/H_2O_2$	$LiBH_4 + 4H_2O_2 = LiOH + B(OH)_3 + 4H_2O$	11.30
CH_4O/H_2O_2	$CH_4O + 3H_2O_2 = CO_2 + 5H_2O$	7.61
Hydrocarbon/H_2O_2	$CH_2 + 3H_2O_2 = CO_2 + 5H_2O$	9.20
N_2H_4/H_2O_2	$N_2H_4 + 2H_2O_2 = N_2 + 4H_2O$	8.18
B_2H_6/H_2O_2	$B_2H_6 + H_2O_2 = 2B(OH)_3 + 6H_2O$	12.14
Otto Fuel II	$C_3H_6N_2O_6 = 3H_2O + 3CO + N_2$	5.04[*]
Li/SF_6	$8Li + SF_6 = 6LiF + Li_2S$	14.47

[*] In a monopropellant configuration.

left out in the list are perchlorates, which will be considered in a separate publication.

Although FC systems involving the use of molecular hydrogen show higher specific energy, it is well known that it is very tough to store gaseous hydrogen efficiently and thus the weight of the practical hydrogen storage system substantially compromises the practical realization of the specific energy. Sodium borohydride water solution and hydrogen peroxide are in a liquid form at room temperature. Thus, $NaBH_4/H_2O_2$ presents a high energy density solution while is convenient for storage and handling.

The products of the $NaBH_4/H_2O_2$ reaction are sodium metaborate and water. These can be stored effectively within the UUV or even discharged safely into sea water. There are no gases such as carbon dioxide that are generated avoiding problems of buoyancy change or noisy gas release. The use of liquid reactants and their ready availability for reaction at the surface of electrodes allow one to achieve good load-following characteristics. Further, the ability to circulate liquid reactants and products presents a convenient method of heat removal from the stack leading to a compact system.

The Otto Fuel II and Li/SF_6 combination have been used on some high speed UUVs (or more precisely naval torpedoes) for sometime. The major problem is that the former is an open cycle system with the associated problems, such as power reduction at depth, noise and so on. The major problem of the latter is the inherent low thermodynamic efficiency associated with the external combustion process and complicated mechanical/maintenance issues.

As a result the highest energy density available for a current UUV is only $600\,\mathrm{Wh\,kg^{-1}}$ system-wise. However, with the advent of $NaBH_4/H_2O_2$ fuel cell technology, this (sometimes psychological) barrier may soon be breached.

4. $NaBH_4/H_2O_2$ FC compared to other options

The direct $NaBH_4/H_2O_2$ fuel cell technology is a nearly ideal solution to meeting the mission requirements of a typical UUV. To understand this, we need to compare it with other technologies envisioned for UUV power systems. All these technologies will be designated by their fuel-storage/oxidizer-storage and energy conversion means. For example, LH_2/LOX, H_2/O_2 fuel cell would denote a power system where the fuel and oxidizer are, respectively, liquefied hydrogen (LH_2) and liquefied oxygen (LOX) and the stored chemical energy is directly converted by a H_2/O_2 fuel cell. Some most likely technical alternatives are listed as follows with the comparison summarized in Table 2.

(1) LH_2/LOX, direct, H_2/O_2 fuel cell
(2) JP8/LOX, reforming, H_2/O_2 fuel cell

Table 2
Comparison of power systems with different fuel/oxidizer and conversion means.

	$NaBH_4$(50%)/H_2O_2(95%) direct, $NaBH_4$/H_2O_2 FC	LH_2/LOX direct, H_2/O_2 FC	JP8/LOX, reforming, H_2/O_2 FC	JP8/H_2O_2(95%), reforming, H_2/O_2 FC	Li/SF_6, direct, Rankine
Energy density as stored, theory	2297 W Hr kg^{-1}, 2986 W Hr l^{-1}	3660, 2086	~2900, ~3100	~2300, ~2990	4019, ~5000
Energy density as stored, real	2182 W Hr kg^{-1}, 2684 W Hr l^{-1}	2928, 1460	1995, 2195	2185, 2840	~3000, ~3800
Conversion efficiency, typical	55%	60%	50%	40%	<25%
Volumetric energy density, overall	1203 W Hr l^{-1}	701	839	828	~700
Mass energy density, overall	1008 W Hr kg^{-1}	1406	924	708	~600
Neutral buoyancy?	Yes	No	Yes	Yes	Yes
Air independent?	Yes	Yes	Yes	Yes	Yes
Scalability	Very Good	Good	Fair	Fair	Poor
Depth independent?	Yes	Yes	No	No	Yes
Rapid start-up?	Yes	No	No	No	Yes
Low observables?	Excellent	Perfect	Poor	Poor	Excellent
Fuel storability	Excellent	Poor	Excellent	Excellent	Excellent
Easy/fast refueling	Excellent	Fair	Excellent	Excellent	Poor
Long hold time	Yes	No	No	Yes	Yes
Non-hull penetration?	Yes	Yes	No	No	Yes
Cost effective?	Yes	No	Yes	Yes	No
Wide operation condition?	Yes	Yes	Yes	Yes	Yes
Shelf life	Long	Long	Long	Long	Long
Safety	Good	Good	Good	Marginal	Good

(3) JP8/H_2O_2 (95%), reforming, H_2/O_2 fuel cell
(4) Li/SF_6, direct, heat engine (Rankine)

The solution based on direct H_2/O_2 fuel cells has to face the problem of gaseous reactant storage, and the storage problem seems insurmountable for an often-demanding UUV power unit. The overall volumetric energy density is rather low if molecular oxygen and hydrogen are to be stored, regardless of the storage means (cryogenic or under pressure). The problem has its root in the large specific volume of molecular hydrogen, which makes its storage intrinsically bulky. This results into the loss of neutral buoyancy, so that the UUV would always float rather than dive. As pointed out by James [10], any H_2/O_2 fuel cell system that directly uses stored molecular oxygen and hydrogen will be hard pressed to achieve the volumetric power density of 1000 Wh l^{-1}. Such an energy density for H_2/O_2 fuel cell requires unrealistic assumptions such as 85% conversion efficiency and zero weight for the FC stack.

When advanced cryogenic storage is used, H_2/O_2 FC may get close to the 1000 Wh l^{-1} target. Such a cryogenic-based power system would nevertheless have very limited mission duration, typically less than 20 days, as witnessed by the Space Shuttle electrical power system [1]. This operational issue makes H_2/O_2 FC less favorable for UUV applications.

H_2/O_2 fuel cells might be fed with reformed hydrogen from hydrocarbon fuel like JP8 and oxygen from LOX, and the stored energy density is high. However, JP8 fuel reformation must be carried out at high temperature, around 1000 °C in some cases. This has significant impact on overall system integration and efficiency. This approach dramatically reduces the overall energy efficiency as a result. It is inherently difficult to thermally integrate a high temperature JP8 reformer with a low temperature fuel cell, such as polymer electrolyte membrane fuel cells. Higher temperature fuel cells such as solid oxide fuel cells (SOFCs) are better choices. However, current technical maturity of SOFC is much lower than the PEM FCs. It is also difficult to clean up the impurities from the JP8 reformates. Notable species are H_2S and CO, which often quickly degrade fuel cell performance. From an operational point of view, the most vulnerable part of such a technology is the handling of CO_2 generated as a product of the FC reaction. The signature/noise left behind by the bubbles of CO_2 released also is undesirable to the UUV. Moreover, a CO_2 release system will unavoidably penetrate the hull of the UUV no matter how perfectly it is engineered,

making system integration difficult. Engineering an acceptable CO_2 disposal system is always a challenge, entailing significant increase in the system size and reduction of system performance.

Similar concerns apply to H_2/O_2 fuel cells consuming reformed H_2 and the O_2 decomposed from H_2O_2. The O_2 decomposition process incurs a performance loss of ~30% compared with a "direct" peroxide fuel cell, making this conversion route rather limited in energy density. This example clearly demonstrates the rationale behind a "direct" fuel cell where reactants are consumed directly at the electrode.

The most recent experiments carried out by the authors also verified the use of ammonia as a stabilizer for $NaBH_4$ in water solution. A slurry type of fuel with mixed $NaBH_4$ and NH_4OH was also tested in a $NaBH_4$/H_2O_2 fuel cell and show very encouraging results. Such a type of slurry has a composition of 50%$NaBH_4$ + 10%NH_3 + 20%NaOH + H_2O-balance.

5. Parametric sizing studies for an exemplary UUV

A UUV would be highly desirable if its power system has the following properties: (1) average power for propulsion/power in the 5–10 kW range, (2) capable of handling short duration (<1% of the overall duty cycle) to peak power levels up to 40 kW, and (3) overall mission duration >30 days. The maximum volume available to house the power plant and energy storage is estimated to be between 4000 and 5500 l.

A preliminary sizing estimate was carried out based on the assumption of having a $NaBH_4$/H_2O_2 FC stack as the power conversion device. The results for this sizing estimate are given in Table 3 below. It is clear that above specification can potentially be achieved with this fuel cell technology, and the estimated energy density is able to approach the pivoting mark of 1000 Wh kg^{-1}.

This sizing estimate assumes that the power output required was 5 kW and requires a mission duration of 30 days. The system could also provide a pulse of 30 kW at a 10% duty cycle. The system weight includes all the major components described in the table (fuel cell stack, a fuel feed and circulation system, a spent fuel collection system, an oxidant feed and circulation system, water separation system, and a thermal control system).

As shown in Table 3, this system will occupy 3591 l of volume and weigh 4288 kg and allow for an additional payload of 696 kg. These results show that the $NaBH_4$/H_2O_2 power source should indeed

Table 3
System sizing and subsystem breakdown for UUV power based on NaBH$_4$/H$_2$O$_2$ Fuel Cell.

UUV system sizing with borohydride/peroxide fuel cell		
Power source sizing inputs		
	Power rating:	5 kW
	Peak:	30 kW, 1% duty
	System control:	10% of total
	Total stacks output	6 kW + 5% allowance
	Total stack output energy for 30 days	4320 kWh
Reactant concentrations		
Oxidizer fuel	H$_2$O$_2$ concentration	95% HTP
	50%NaBH$_4$ + 10%NH$_3$ + 20%NaOH solution	
	Energy density at 55% efficiency + 90% utilization	1.136 kWh kg^{-1}
Fuel cell stack specs		
Stack operation point	EMF	2.25 V
	Cell open circuit voltage	1.4 V
	Cell operational voltage	1.23 V
	Efficiency	55%
	Current density at 55% efficiency	100 mA cm^{-2}
	Total output voltage	200 V
Subsystem sizing		
Stack sizing	Stack cell number	165
	Stack current	29 A
	Active area per cell	300 cm^2
	Stack cross-section with integrated manifold	800 cm^2
	Thickness, each cell	4.5 mm
	Bipolar plate composition	Polymer + stainless Steel
	Stack, overall length	770 mm
	Stack, overall volume	61.6 l
	Stack, weight	145 kg
Reactant sizing		
	Total reactant mass	3802.8 kg
	Mass, oxidizer	2578.2 kg
	Mass, fuel	1224.6 kg
	Volume, oxidizer	1895.7 l
	Volume, fuel	1224.6 l
Reactant + Storage	Mass (5% structural)	3993.0 kg
	Volume (10% structural)	3276.4 l
Reactant circulator/dilutor/conditioner		
	Mass	50 kg
	Volume	30 l
Fuel cell system controller/power conditioner		
	Mass	25 kg
	Volume	20 l
Secondary battery for startup/EPS		
	Mass	25 kg
	Volume	20 l
Startup water storage		
	Mass	25 kg
	Volume	22 l
Propulsion motor + power train		
	Mass	25 kg
	Volume	10 l
Overall power/propulsion system		
	Mass	4288.0 kg
	Volume (10% packing space factor)	3612.0 l
Overall power/propulsion system		
	Mass energy density	1007.5 Wh kg^{-1}
	Volumetric energy density	1196.0 Wh l^{-1}
Main structural factor, overall UUV system HY-100 steel		
300 meter safe diving	Mass	670 kg
	Volume	5500 l
	Volume equivalent mass for neutral buoyancy (Sea water SG: 1.028)	5654 kg
	Additional payload	696.0 kg

be considered as a serious candidate for future UUV program. The NaBH$_4$/H$_2$O$_2$ FC power system has a projected power density of 1008 Wh kg^{-1} and 1196 Wh l^{-1}, respectively.

6. Experimental

Note that the parametric system sizing of Table 3 is based on very conservative assumptions on the NaBH$_4$/H$_2$O$_2$ cell performance in terms of open circuit voltage and power density. The current borohydride/peroxide cell performance is higher. The authors have found that the power density of NaBH$_4$/H$_2$O$_2$ cell can be increased by two unique treatment and operation approaches.

The catalytic diffusion electrodes (layers) of the NaBH$_4$/H$_2$O$_2$ fuel cell are typically made by an electro-deposition method [4]. It is often deposited in a separated electrochemical cell before being assembled into the NaBH$_4$/H$_2$O$_2$ cell. Two problems are found in such a method. First, the catalyst distribution formed on the carbon diffusion layers does not necessarily conform to the ionic channel of the Nafion membrane, contributing to a significant loss during operation. Second, the electrodes, especially the cathode side, often experience significant performance loss after several hundred hours of operation. It is inconvenient to dissemble the cell and electroplate the electrode again. Therefore, an in-situ electroplating technique was developed to solve the two problems, without the potential trouble of taking a stack apart. As an example, we discuss how gold is in-situ deposited on the cathode.

Gold is the material of choice for the H$_2$O$_2$ cathode due to its stability. After a porous carbon diffusion layer is ex-situ electroplated, it is assembled in to fuel cell as the cathode, as in the ordinary procedure. The in-situ plating then starts here. To do this, the anode chamber will be circulated with 5-wt% HCl solution in water, while the cathode chamber will be pumped with a 0.1-wt% KAuCl$_4$ (potassium tetrachloroaurate) water solution. Anode and cathode here, respectively, refers to the fuel electrode and oxidizer electrode in the galvanic mode, but not those in the electrolytic cell mode during the in-situ electroplating process. Hydrochloric acid is used here to increase conductivity. To initiate electroplating, we apply a positive voltage to the cathode chamber and the negative side to the anode chamber. The applied voltage is typically around 1 V. Such a voltage is large enough to reduce the Au from the KAuCl$_4$ solution while still low so as not to cause corrosion problems to other part of the fuel cell. As a result, Au preferably deposits to the side of the cathode diffusion layer immediately in contact with the Nafion PEM. The flow and diffusion of the KAuCl$_4$ is similar to that to be encountered by H$_2$O$_2$ in the real fuel cell operation, and therefore the location and nucleation of Au is automatically optimized. The amount of deposition can be loosely controlled by the color change in the KAuCl$_4$ solution: a colorless clear solution tells that KAuCl$_4$ are used up. More precise control can be affected by quantitative control of the initial solution concentration and amount. Similar principle applies to the in-situ plating of Pd for the catalytic anode side. The catalyst loadings are all 5 mg cm^{-2} through out research reported here.

Performance from the ordinary ex-situ plating and the much-improved in-situ plating are summarized in Figs. 1 and 2. The active area of the fuel cell is 25 cm^2 for both cases. Fig. 1 gives the performance curves for ordinary electroplating technique. Preliminary analysis of similar data was published elsewhere [11]. Here the data are closely inspected and divided into two temperature regimes. The temperature measurement was carefully calibrated so that it is now fixed to 60 °C as oppose to previous estimate of approximately 50 °C.

The in-situ electroplating significantly improves ionic conduction and catalytic effectiveness at high current density. Compared to Fig. 1, the test shown in Fig. 2 had a current scanned down to
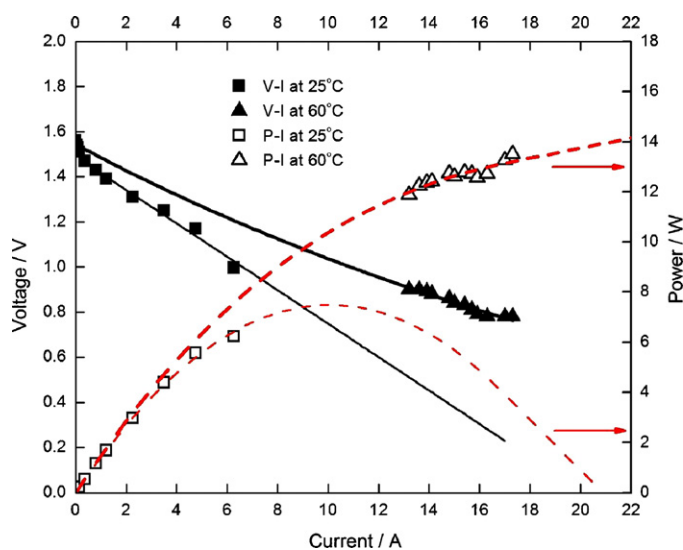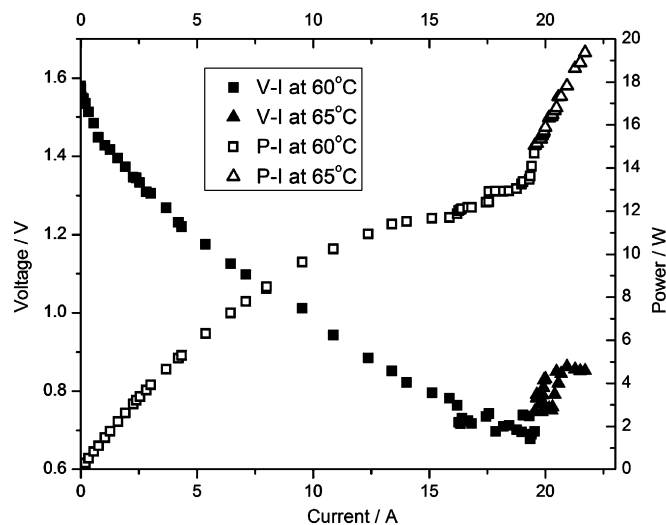
Fig. 1. Voltage–current and power–current properties of a typical fuel cell without in-situ electroplating. The lines are fitted to the data points and serve as guide to the eye.

Fig. 3. Voltage–current and power–current properties of a fuel cell with Pd as the cathode catalyst and Au as the anode catalyst. The fuel cell is in-situ electroplated.
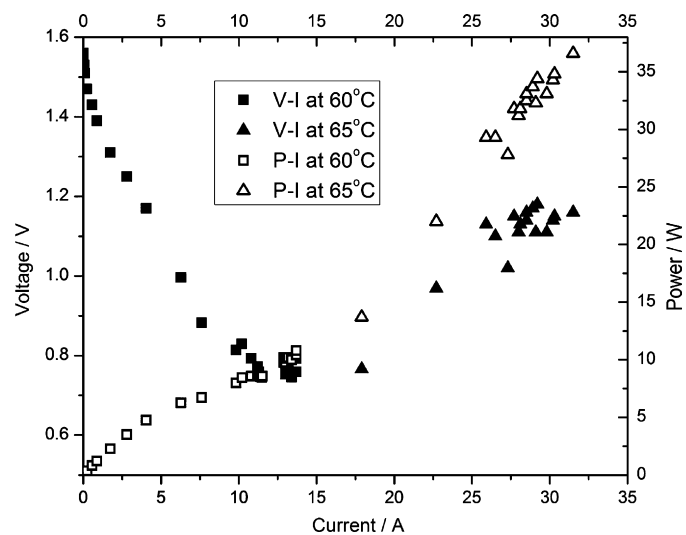
zero at 60 °C. Then the current was hold near 20 A for a minute or so. The power output at this current is roughly 15 W with even more wattage of waste heat generated. The generated heat is so intense that it over-powers the temperature control mechanism and the cell was quickly heated up to around 65 °C. The triangular shaped data were taken during the heat-up process. The cell therefore tends to run-off when the resistance of the external load is lowered. These tendencies, however, can be readily controlled by simply reducing the current with the increase of external load resistance. The maximal power recorded is over 19 W. In all these tests, the cell was not externally heated or pressurized.

The in-situ electroplating process on average improves the power density by roughly 20–40% depending on a number of factors, such as temperature, the type of carbon diffusion layer, and so on. A systematic investigation is highly desired in the future. The maximal power density obtained with this method is roughly 0.77 W cm^{-2}, at a cell voltage near 0.87 V.

In further pursuit of even higher power density, we came up with another simple yet effective approach. Acid stabilized hydro-

gen peroxide seems too stable with a gold-based catalyst. There was no visible sign of decomposition whatsoever, in the cathode chamber, even under heavy load. This is in sharp contrast to the borohydride side, where small amount of hydrolysis always occurs in contact with palladium. A search in the literature quickly found that Pd had long been used as a potent catalyst for hydrogen peroxide [12], which corroborated to our previous experience that it tends to be too active for non-stabilized peroxide. Therefore, one simple way to really increase the power density would be to use Pd for the reduction of peroxide while using gold for the borohydride oxidization. This can be readily achieved by swapping the fuel and the oxidizer side of the fuel cell. The result was phenomenal.

Compared to Fig. 2, the swap of fuel and oxidizer reduced the power at the relatively low current density. However, when the current was increased to nearly 20 A the cell quickly heated up. The power output at this current was again roughly 15 W with even more wattage of waste heat generated. The generated heat was enough to heat the cell over 65 °C on short notice. The triangular data in Fig. 3 were then quickly recorded over a period of ∼40 s. The maximal power was over 36 W, translating into a power density well over 1.5 W cm^{-2}. Once again, we see run-off phenomenon similar to that in Fig. 2, but with much larger magnitude. The test demonstrated more active catalytic nature of Pd on peroxide compared to Au. This improvement, however, was obtained at a price: the direct decomposition of the peroxide is now apparent, evident by the bubbling in the peroxide side of the fuel cell. The bubbles of gaseous oxygen are formed from the peroxide decomposition.

Fig. 3 is typical of the I–V curves of this type of fuel cell with in-situ electroplating. The cell voltage first decreases with the cell current from 0 A to 15 A. It then increases with the increase in the cell current from 15 A to 30 A. This behavior is different from typical fuel cell polarization curves. One possible mechanism attributes this behavior to nano-particles clogging the micropores of the Nafion membrane when it is partially electroplated during the in-situ electroplating process. The nano-particles block some micropores of the Nafion membrane at low temperature and low current. When the temperature and current increase, the micropores swell accordingly due to thermal expansion, as well as the pressure change due to the electro-osmotic flow. Beyond a certain point, the prior clogged micropores open up, forming ionic conductive channels. The internal resistance of the PEM is therefore reduced. The reduction in the internal resistance is reflected in one

Fig. 2. Voltage–current and power–current properties of a typical fuel cell with in-situ electroplating.

part of the fuel cell polarization curve as cell voltage increases with the current. Of course, this only occurs in a limited current range.

The application of the in-situ electroplating technique is not limited to a borohydride/peroxide fuel cell. In principle, it can be applied to any direct liquid fuel cell. One of the authors (NL) has adopted it to a direct methanol fuel cell with encouraging results. This is to be discussed in a separate publication.

7. Conclusion

Theoretical studies of $NaBH_4/H_2O_2$ for air independence power systems were carried out, with emphasis on underwater propulsions. The borodydride/peroxide combination and the direct fuel cell approach were compared to a number of other options. The result of the parametric studies clearly demonstrates the promise of such a technology. It offers neutral buoyancy, closed-cycle, depth independence and very silent operation, essential for high performance UUVs. Experimental studies to improve the power density of the $NaBH_4/H_2O_2$ fuel cells were also carried out. One notable achievement is the adoption of the in-situ electroplating technique to increase the cell performance by an average 30%. Also demonstrated is the catalytic power of Pd for peroxide reduction at the cost of increasing the direct decomposition of H_2O_2. Such a side-effect could be addressed in future by properly alloying Au with Pd.

Acknowledgments

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