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Hydrogen-Peroxide-Based Fuel Cells for Space Power Systems

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A fuel cell using nontraditional fuel and oxidizer is investigated in this research. H_2O_2 is used in this unique fuel cell directly at the cathode. Two types of reactant, namely, a gas-phase hydrogen and an aqueous $NaBH_4$ solution, were used as fuel at the anode. The direct utilization of H_2O_2 and $NaBH_4$ at the electrodes, as seen in experiments, results in >30% higher voltage output compared to the ordinary H_2/O_2 fuel cell. Further, the unique combination of $NaBH_4$ and H_2O_2, both of which are in an aqueous form, has numerous advantages from an operational point of view. This design is inherently compact compared to other cells that use gas-phase reactants. Consequently, the peroxide-based fuel cell is well suited for space power applications where air is not available and a high-energy density fuel is essential.

Nomenclature

A = active area per unit mass, m^2/kg
E_V = reversible open-circuit voltage, V
I = discharge current density, A/m^2
M_F = mass of fuel, kg
M_S = mass of FC stack, kg
P = output power, W
t_d = discharge time, h
V = discharge voltage, V
α = concentration of reactants in solution, %
η_D = discharge energy conversion efficiency, %
η_e = energy conversion efficiency, %
μ_f = reacted fuel coefficient, %
ξ = theoretical energy output, $W \cdot h$
ρ_E = specific energy density, $W \cdot h/kg$
ρ_F = fuel specific power density, W/kg
ρ_P = specific power density, W/kg
ρ_S = stack specific power density, W/kg

I. Introduction

HYDROGEN peroxide (H_2O_2) is commonly used as an oxidizer in rocket propulsion and air-independent power systems. One of its earliest applications for aerospace propulsion was found on the Mescherschmitt ME-163 "Komet" rocket plane. It is also widely used for underwater power systems [1] and has a number of desired properties as an energetic material.

H_2O_2 is a powerful oxidizer. Through catalysis, H_2O_2 can be converted into hydroxyl radicals ($OH^{\cdot}$) with reactivity second only to fluorine. By using catalysts such as Fe^{2+}, H_2O_2 can be readily converted into hydroxyl ion (OH^-), which makes it a desired reactant for a fuel cell (FC). Combined with different fuels, H_2O_2 forms a potent rocket propellant. With hydrogen the specific impulse is over 322 s in vacuum [2]. H_2O_2 is also a natural metabolite of many organisms. When decomposed it gives only oxygen and water. H_2O_2 can be formed by the action of sunlight on water, a purification system of nature. Consequently, H_2O_2 has none of the environmental problems associated with many other chemical oxidizers. Last but not least, H_2O_2 is now produced at over a billion pounds per year; the high volume production results in very low cost.

Recently there has been a revived interest in using H_2O_2 for aerospace power applications, as witnessed by a number of recent publications [3]. The revival was prompted by environmental concerns and accelerated by the dropping price of H_2O_2.

The use of hydrogen peroxide in FCs is a relatively recent development, however. Some peroxide-based semi-FC devices using Al for the anode were investigated elsewhere [4–7]. Very recently, full fuel cells based on H_2/H_2O_2 and on $NaBH_4/H_2O_2$ have been reported as well [8–12]. Studies [3] have shown that bioelectrocatalysts (BEC) can electrocatalyze the reduction of hydrogen peroxide without appreciable peroxide decomposition, although the FC based on BEC works at relatively low current and power density. All these results have shown the general feasibility of a peroxide-based electrochemical cell. A typical FC uses air as the oxidizer and therefore H_2O_2 was not studied for applications where air is readily available, such as ground transportation. However, for space or underwater applications, H_2O_2 based systems (whether heat engine or FC based) are an ideal choice. The reasoning for this will be further delineated next.

Space applications require high power/energy density and air independence. Chemical power systems therefore should adopt energetic materials similar to rocket propellants. Typical oxidizers used in rocket propellants are liquid oxygen (LOX), and to a lesser extent, N_2O_4. The use of N_2O_4 in a FC should be very restricted because of its extreme toxicity. LOX is environmentally sound, but is not suitable for long-time storage due to its vaporization. The Dewar lifetime for 1 ton of LOX is only on the order of 1 month, while most satellites today call for a mission duration of several years. Bottled

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high-pressure oxygen is not an ideal option either because its storage efficiency is rather low (often ~0.3 kg/l).

In comparison, H_2O_2 is an ideal option. It is storable as long as overheating is avoided. It is biologically sound and environmentally compatible. The energy density of concentrated H_2O_2 is also very high. When used in a FC at the cathode, it is readily catalyzed in a controlled reduction and greatly enhances the overall FC efficiency. Control of output power can simply involve changing the concentration of the aqueous H_2O_2 solution. Thus, short-time overloading or pulsing can be achieved by increasing the H_2O_2 concentration at the cathode side.

The benefits of a direct H_2O_2 FC compared to cells using gaseous oxygen are manyfold as follows:

Higher current density from larger oxidizer mass density: In a conventional FC, oxygen joins the reduction reaction in a gaseous form. Because the mass density in a gas phase is ordinarily 1000 times less than in a liquid phase, peroxide fuel cells have the potential for a higher area current density (a volume density difference of 1000 times translates into an area density difference of 100 times). The relatively low diffusivity of a liquid compared to a gas reduces the advantage to a certain degree. Still our experiments indeed demonstrated power densities difficult to achieve for a gaseous fuel cell without pressurization and heating.

Single-phase transport on the cathode side of FC increases reaction rate: In a traditional FC the mass transport of reactant is a two-phase process. In a proton exchange membrane fuel cell (PEMFC), in particular, the two-phase transport of reactant and product species is known to be the limiting phenomenon of PEMFC operation [13–16]. Furthermore, water generated in the cathode reaction can condense and block the open pores of the gas diffusion layer, limiting reactant transport. By shifting to a liquid phase reactant, the direct H_2O_2 FC largely bypasses these transport problems.

Eliminating the O_2 reduction overpotential problem: The slow kinetics of oxygen reduction has long been known as the single largest factor limiting the current density, power density, and the overall energy conversion efficiency of an oxygen FC system. The oxygen reduction reaction at the cathode is written as

$$O_2 + 4H^+ + 4e \rightarrow 2H_2O$$

This reaction involves the simultaneous transfer of four electrons, and therefore has a low probability of occurrence [17,18]. A high cathodic overpotential loss of 220 mV while operating close to the open-circuit voltage has been observed in state-of-the-art Pt loading electrocatalysts, for net current density approaching zero. This is due to a mixed potential that is set up at the oxygen electrode. The mixed potential is from a combination of slow O_2-reduction kinetics and competing anodic processes such as Pt-oxide formation [19,20]. It has been determined that the exchange current density of O_2 reduction is 6 orders of magnitude lower than that of H_2 oxidation [21]. In comparison, the H_2O_2 reduction process at the cathode,

$$H_2O_2 + 2e \rightarrow 2OH^-$$

is a two-electron-transfer process involving a much lower activation barrier. This improvement therefore circumvents the overpotential problem of a H_2/O_2 fuel cell.

Of course, hydrogen peroxide is rarely available in 100% concentration. However, high test peroxide (HTP) with concentration greater than 85% is readily available and has been successfully adopted for rocket propulsion, for example, in the British Black Arrow launch rocket. Even at the modest concentration of 85% peroxide, the H_2/H_2O_2 (2728 $W \cdot h/kg$ if pure) combination has a gravimetric energy density at least 70% higher than that of H_2/O_2(gaseous) (3660 $W \cdot h/kg$ if pure) even when the latter is stored in the state-of-the-art graphite fiber reinforced composite pressurized vessels. The improvement in the volumetric energy density enabled by peroxide is even more prominent, being typically 5 times compared to the standard pressurized oxygen system at 20 MPa.

II. Experimental Setup and Results

A series of small proton exchange membrane (PEM) peroxide fuels cells were fabricated for this research. The use of a PEM instead of a liquid electrolyte makes the FC compact and relatively maintenance free. Also, the PEM design significantly reduces reactant crossover which can be severe if a liquid electrolyte is used.

A. Fabrication of the Peroxide Fuel Cell

The prototype peroxide fuel cells differ from normal H_2/O_2 fuel cells mainly in the membrane electrode assembly (MEA). The fabrication of the MEA starts with the catalyst ink. Carbon-supported Pt catalyst (Alfa Aesar 40%-wt Pt on Cabot XC-72) powder is first homogeneously dispersed in isopropanol, which is then mixed with 5%-wt Nafion solution. The ink is then brushed onto a piece of carbon paper (Toray) or carbon cloth (E-Tek), which acts as a reactant diffusion layer. Note that the carbon substrate here is termed "reactant diffusion layer" (RDL) instead of the often-cited "gas diffusion layer" because most of the peroxide FC reactants are in liquid phase. The diffusion layer used for the H_2 anode takes one more step to prepare: it needs to be water proofed by using Teflon. The catalyst coated diffusion layers, which will later be called reactant diffusion electrodes (RDE), are then dried out in an oven at 80°C for 1 h. The effective loading of the catalyst is maintained at 1 mg/cm^2 throughout the studies. The liquid phase RDE differs significantly from the traditional gas diffusion electrode (GDE) of an ordinary gas fuel cell in that the RDE is highly hydrophilic. To ensure this, ordinary Teflon binders cannot be used and the amount of Nafion solution as a binder is strictly regulated. The RDE once made is to undergo hydrophilic tests. If the RDE is not hydrophilic enough it will be plasma treated in a vacuum chamber under an oxygen glow discharge. Such a treatment typically lasts for 140 s and is carried out at a partial oxygen pressure of 0.53 Pa (4 mTorr).

A Dupont Nafion 112 membrane is used as the electrolyte. It was boiled in an aqueous solution of 3%-wt H_2O_2 + 3%-wt H_2SO_4 for 1 h before rinsing in deionized (DI) water for 2 h. The Nafion PEM is then activated by 0.5M H_2SO_4 for 2 h, followed by a triple rinse in DI water.

The activated Nafion PEM is then held together by two reactant diffusion electrodes and hot bonded together at 125°C, under a pressure of 1000 psi. This hot pressing typically last about 30 s and is the final step in the fabrication of MEA.

The MEA is then sandwiched between two perforated stainless steel plates, which act as an electrical contact, while permitting the permeation of reactants. The whole assembly is fastened together with the help of bolts, nuts, and two polycarbonate end plates. A liquid-tight seal is formed by a silicone elastomer.

B. Performance of Peroxide FC

Liquid reactants, namely, water solutions of $NaBH_4$ and H_2O_2, were circulated by a Cole–Parmer diaphragm pump, at a flow rate of ~40 cm^3/min. The $NaBH_4$ fuel used in the anode is a 20%-wt aqueous solution stabilized with 1.8 M potassium hydroxide (KOH). The cathode side used 20%-wt water solution of hydrogen peroxide stabilized with 5%-wt phosphoric acid. Gas-phase hydrogen was generated by an electrolyzer and used to feed the H_2 anode in the H_2/H_2O_2 FC. The V–I characteristic curves of both FCs were measured by discharging the cell using a variable load. The voltage and current were logged by an HP 34970A data acquisition system. The typical V–I curves of the peroxide FCs are given in Fig. 1 along with those of traditional H_2/O_2 FCs for comparison. The H_2/O_2 FC performance data are from [22,23].

There are a few observations worth mentioning. First, both peroxide fuel cells have a higher open-circuit voltage than that of a typical H_2/O_2 PEM FC (<1 V). This is to be expected because both have fairly high thermodynamically reversible open-circuit potential:

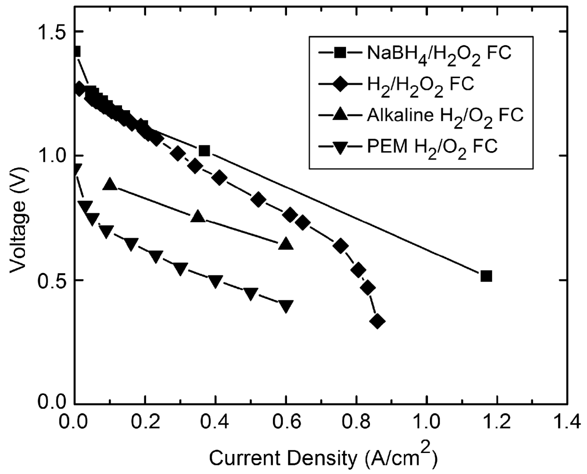

Fig. 1 The *V–I* characteristics of various FCs at room temperature, and ambient pressure operation. Note the prominent H_2O_2 FC performance. The curve for the H_2/H_2O_2 fuel cell is tested with a pH = 2 catholyte.

$$H_2 + H_2O_2 \rightarrow 2H_2O, \qquad 1.78\text{ V}$$

$$NaBH_4 + 4H_2O_2 \rightarrow NaBO_2 + 6H_2O, \qquad 2.25\text{ V}$$

Second, the open-circuit voltage, in both cases, is higher than the 1.23 V ideal potential of a hydrogen/oxygen FC. This is an unambiguous evidence for the "direct" reduction of hydrogen peroxide at the cathode. Third, although the absolute cell voltage is high for the particular peroxide FCs shown in Fig. 1, it is not very impressive compared to the theoretical potential. For example, the 1.4 V open-circuit voltage (OCV) of the $NaBH_4/H_2O_2$ FC in Fig. 1 is only 62% of that theoretically achievable. This was likely due to some crossover of peroxide to the anode side, even with the use of a Nafion PEM. This is a disadvantage brought forward by a hydrophilic liquid phase reactant. Follow-on research has been specifically carried out to address such issues. The latest peroxide fuel cells now receive special treatment to stop the crossover. Combined with improvement in catalyst research, an OCV of 1.87 V was achieved at ambient pressure and temperature. This corresponds to an efficiency of 83%, as shown in Fig. 2 of [24]. Note that this efficiency is reached after the additional loss due to the overpotential of the $NaBH_4$ anode, which, unlike a hydrogen anode, incurs nonnegligible anodic overpotential. In comparison, a state-of-the-art H_2/O_2 cell barely reaches 1.0 V OCV (81%) at ambient pressure/temperature, even when the H_2 anode overpotential is negligible. These are unambiguous indications that the peroxide cathode indeed has lower overpotentials, at least on a percentage base, when compared to the oxygen one.

It is also interesting to compare the current results to previous ones [11,12], which are of related design. Some differences in the two prevent a direct comparison, however. A predominately rare Earth alloy is used in the IIS anode while the current type adopted carbon-supported platinum. The IIS catholyte is strongly acidic with a pH value near 0. The electrochemical potential of a redox reaction is strongly affected by the pH. For example, the cathode potential and the catholyte pH are directly related in a peroxide FC by

$$E_V(H_2O_2) = 1.78 - 0.059\ \text{pH}$$

The latter fact alone should boost the open-circuit voltage by some 0.4 V compared to a cell using catholyte of pH = 7, which is the current case. Therefore, the difference in open-circuit voltage of the two experiments can largely be attributed to the strongly acidic catholyte used in the IIS experiment. The remaining difference of some 0.1–0.2 V can be explained by a more negative electrochemical potential of the rare Earth alloy. On the electric current density and power density side, our results appear several times higher than the IIS results, possibly due to Pt catalysts used in the anode, which are electrochemically more active.

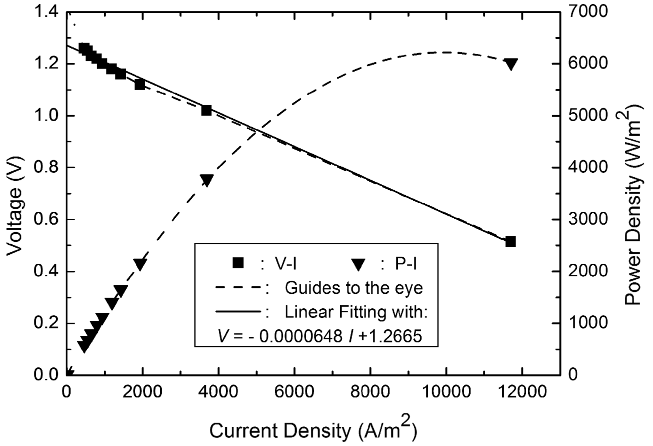

Fig. 2 Experimental performance of the $NaBH_4/H_2O_2$ FC and a linear fit.

The theoretical potential of the $NaBH_4/H_2O_2$ electrochemical couple is around a full 1 V higher than the standard potential of a H_2/O_2 FC (1.23 V). This translates into a significant reduction in the number of stages needed for a practical FC stack design and therefore produces a decisive advantage from an operational point of view. As shown in Fig. 1, the peroxide-based FCs (both H_2/H_2O_2 and $NaBH_4/H_2O_2$) indeed offer higher voltage and current density than obtained from traditional FCs at similar conditions.

Experimentally, a power density of 0.6 W/cm^2 was achieved with the H_2/H_2O_2 FC while the $NaBH_4/H_2O_2$ FC reached 0.8 W/cm^2, both at room temperature and ambient pressure. These quoted numbers refer to the peroxide fuel cells that use carbon-supported platinum catalysts at the electrode listed in Table 1. For the peroxide FC using BEC at the cathode, the power density is usually on the order of 1–10 mW/cm^2.

The experimentally achieved energy density is around 1000 W · h/kg, which is significantly higher than that of ordinary batteries. This opens up a range of possible applications other than the space type. For example, the current and projected power requirements for mobile applications could benefit from the high theoretical power densities of the $NaBH_4/H_2O_2$ fuel cell technology. Batteries currently power a myriad of mobile equipment (sensors, communications, portable devices, etc.). However, government-sponsored research across the world is developing new equipment hungry for power. A mean power requirement of 20 W for a 72-h application would equate to an energy requirement of 1.44 kW · h. Current battery technologies ($Li/SOCl_2$ and Li/MnO_2, for example) involve a weight penalty of approximately 200–400% (5.14 and 9.94 kg total system weight, respectively, compared to a hydrogen fueled PEM fuel cell with the hydrogen fuel stored at 5000 psi (2.09 kg system weight). The associated energy densities equate into 280 W · h/kg for the Li primary battery, 145 W · h/kg for the Li/MnO_2 battery, and 1034 W · h/kg for a typical PEM system (the PEM system was evaluated at 30 W mean output and 2160 total W · h). It is generally true that longer mission times and higher energy requirements would favor a fueled system over batteries.

Table 1 Performance of peroxide FCs at 1 atm and 300 K

Type	Ideal energy density, W · h/kg	Voltage (open circuit)	Current (short circuit)	Max. power density	Efficiency @ 100 mA/cm^2
H_2/H_2O_2	2728	>1.05 V	>1.8 A/cm^2	>0.6 W/cm^2	>55%
$NaBH_4/H_2O_2$	2580	>1.40 V	>3.0 A/cm^2	>0.7 W/cm^2	~55%

Consequently, the $NaBH_4/H_2O_2$ fuel cell technology described in this paper could be a viable solution for the ever-increasing power requirements of the dismounted infantry, given a threefold higher energy density than the best lithium battery.

The energy density in Table 1 is based on the assumption of 100% fuel utilization. In reality the fuel cannot be fully consumed and this reduces the actual energy density that can be achieved. However, for the borohydride/peroxide fuel cell, the fuel utilization is typically over 90%. The borohydride/peroxide fuel cells at the authors' laboratory are typically benchmarked at 10% H_2O_2 and 10% $NaBH_4$ and they still run on concentration down to 5%. Higher concentration gives higher power density, but the power increase levels off if the concentration is over 30%. The power density improves by ~60% going from 10 to 20% in concentration, and another ~15% from 20 to 30%. In summary, the fuel utilization of the peroxide fuel cell system is fairly high at over 90%.

With the use of all-liquid reactants in the borohydride/peroxide FC, the fuel/oxidizer management becomes a very simple task, so the storage can be kept light and compact. First, no water humidifier is needed because the Nafion PEM is 100% saturated with water. Secondly, the liquid reactant offers a fairly large heat removal capacity so that a separate liquid cooling loop is not needed even for high power stacks. This liquid form reactant therefore possesses some decisive advantages over the gas-phase hydrogen used in the H_2/H_2O_2 and conventional H_2/O_2 FCs.

The use of all-liquid reactants also resolves a number of issues limiting efficient regenerative operation in other fuel cell systems. There have been a number of prior efforts to achieve a regenerative fuel cell (RFC). In the traditional design, the handling and storage of gas-phase reactants, namely, H_2 and O_2, has long been the hurdles limiting the performance of RFC. In a typical H_2/O_2, a delicate and conflicting balance of hydrophilic and hydrophobic treatments is required to maintain the fragile three-phase (gas–liquid–solid) interface. For effective regeneration, hydrophilic electrodes are preferred, while for discharge operation a typical FC needs hydrophobic gas diffusion layers. This conflicting requirement makes a unitized design extremely difficult for a H_2/O_2 RFC, forcing separate units for these functions. Another issue in unitized design for H_2/O_2 RFCs is the huge overpotential (0.4 V) involved in both oxygen reduction and generation. A single material is very difficult to function as both an O_2 evolution and reduction electrodes. In contrast, a $NaBH_4/H_2O_2$ cell bypasses both problems. Thus, a unitized RFC appears quite feasible for a $NaBH_4/H_2O_2$ fuel cell, and initial experiments in that direction are quite encouraging. Indeed, the very first regenerative operation in a prototype $NaBH_4/H_2O_2$ FC has reached an energy density of 65 $W \cdot h/kg$, with enormous potential for future growth. The details of this unitized $NaBH_4/H_2O_2$ RFC will be separately discussed in a future publication.

C. Performance Summary

In summary, there are a number of prominent features that distinguish the $NaBH_4/H_2O_2$ FC from the H_2/O_2 ones and conventional batteries. From a performance point of view, space power systems based on an open-cycle $NaBH_4/H_2O_2$ FC have the following distinct advantages:

1) very high energy density (over 2580 $W \cdot h/kg$ theoretical, over 1000 $W \cdot h/kg$ achieved experimentally, nearly *10* times higher than current state-of-the-art batteries used for space applications;

2) very high volume power density because of the direct utilization of H_2O_2 at the cathode;

3) the ability to overload for a short period of time simply by increasing the concentration of H_2O_2 at the cathode;

4) the potential for a very high efficiency (over 60%) because the use of H_2O_2 overcomes the oxygen overpotential problem inherent to prior H_2/O_2 FC designs.

As for the regenerative (closed-cycle) operation, this FC technology has the following distinct merits:

1) high gravimetric (mass) energy density of 65 $W \cdot h/kg$ proved, and potentially 125–200 $W \cdot h/kg$; both nominal and on orbit;

2) much improved low Earth orbit (LEO) and medium Earth orbit (MEO) cycle performances; LEO/MEO performance is at least 3 times higher than the current state-of-the-art lithium batteries;

3) fast discharge/recharge properties, as required by LEO/MEO operation, and preferred by future high power missions;

4) very long cycle life due to the catalytic electrode design.

From an operational point of view the $NaBH_4/H_2O_2$ FC has the additional benefits:

1) environmentally safe;

2) long-time storage of energetic materials;

3) low operational cost.

The abovementioned advantages open up a number of operation scenarios for novel space power systems. An ideal application is to power space-borne directed energy beam systems. Such a typical system requires a peak power level of 100 kW, for a short time, at a mass constraint of around a few tons and a service life of a few years. This is clearly out of reach for current battery and conventional FC technology. Take the space shuttle power system as an example. Typical alkaline FCs using cryogenic hydrogen and oxygen are at the heart of the space shuttle power system. The mission duration of the space shuttle has never been over 20 days. This short duration is primarily limited by the sustainability of the liquid hydrogen storage. Another scenario consists of powering a rover on the lunar surface. The Apollo-type rovers had electric motors totaling some 1 kW. Its energy storage consists of primary battery cells. The typical energy density for such batteries is on the order of 100 $W \cdot h/kg$. Using the nonregenerative $NaBH_4/H_2O_2$ FC could readily extend the rover mission range by a factor of 5–10.

In the following section, we will review a parametric study of the performance of this FC for such applications.

III. Performance Study of Peroxide FC Applications

A. Generalized Parameterization

Similar to [25], a mass-power model for a liquid reactant FC can be characterized in a manner analogous to a battery. The main components of a liquid FC are the reactants and the FC stack. Other smaller subsystems such as fuel tanks, cell casings, and pumps can, to the first order, be neglected in evaluation of the system mass. Then the power delivered by the FC, P, divided by this mass estimate (M_F for fuel and M_S for stack), gives the specific power density ρ_P:

$$\rho_P = \frac{P}{M_F + M_S} \tag{1}$$

Then, the specific energy density ρ_E is given by

$$\rho_E = \rho_P t_d \tag{2}$$

where t_d is the fuel cell discharge time.

Rewriting the right-hand side of Eq. (1), the cell specific power density, ρ_P, is obtained in terms of the fuel specific power density, $\rho_F = P/M_F$, and the stack power density, $\rho_S = P/M_S$:

$$\rho_P = \frac{1}{(1/\rho_F) + (1/\rho_S)} \tag{3}$$

The fuel specific power density can also be characterized by

$$\rho_F = \frac{E}{t_d M_F} \tag{4}$$

where E is the total energy output.

Rewriting Eq. (4), in terms of the energy conversion efficiency, η_e, we obtain

$$\rho_F = \frac{\eta_e \xi}{t_d M_F} \tag{5}$$

where ξ is the theoretical energy output while η_e denotes energy conversion efficiency.

The theoretical energy output for hydrogen peroxide/sodium borohydride is 2580 $W \cdot h/kg$ of reactants (using 2.25 V as the 100%

voltage efficiency of the fuel cell). In practice, we need to take into consideration the solution concentrations. Thus α is now introduced, which represents the percent concentration of the reactants in solution. Equation (5) can now be rewritten as

$$\rho_F = \frac{2580\eta_e\alpha}{t_d} \tag{6}$$

Since only open-cycle fuel cells are being considered here, η_e is equal to the discharge energy conversion efficiency η_D, or

$$\eta_e = \eta_D \tag{7}$$

Taking into account the percentage of reactants that is consumed during discharge (ideally 100%), we now introduce the reacted fuel coefficient, μ_f, and write the discharge efficiency η_D as

$$\eta_D = \mu_f \frac{V}{E_v} \tag{8}$$

where V is discharge voltage (V) and E_V represents the reversible OCV (V).

By using the OCV for $NaBH_4/H_2O_2$ FC of 2.25 V, Eq. (8) can be rewritten as

$$\eta_D = \frac{V\mu_f}{2.25} \tag{9}$$

Thus, combining Eqs. (6), (7), and (9) gives

$$\rho_F = \frac{1147V\mu_f\alpha}{t_d} \tag{10}$$

Equation (10) represents the contribution of the fuel (reactant solutions) to FC power density. Finally, the stack specific power density, ρ_S, can be rewritten in terms of the active area per unit mass A, and discharge current density I for a given voltage V:

$$\rho_S = VIA \tag{11}$$

The active area per unit mass simply represents the specific active area, or the active area of the FC stack per unit mass. At this point the generalized equations for a mass-power model have been presented. This generalized parameterization shall be developed further and applied to open-cycle H_2O_2 fuel cells as follows.

B. Open-Cycle Peroxide Fuel Cells

By combining Eqs. (3), (10), and (11), the following is obtained:

$$\rho_P = \frac{V}{(t_d/1147\mu_f\alpha) + (1/IA)} \tag{12}$$

Now, to evaluate Eq. (12) the relationship between voltage (V) and current (I) obtained from experimental data in Fig. 2 will be used. Also shown in Fig. 2 is a representation of the test data using a linear fit within a limited range of operating parameters, and the experimental values for power densities. Although not exact, this linear model is acceptable for the range of current densities that are of concern: 1000–12000 A/m^2. Below this range, less than 1000 A/m^2, the power density is too low, forcing the FC stack to increase in size, causing the system mass to increase. Above this range ($>12,000$ A/m^2), the efficiency is too low, forcing more fuel to be used than necessary, and once again increasing the system mass. Essentially the optimal system size (lowest possible mass for mission profile) is obtained between these values of current density.

From this linear model the following representation for V (volts) of the FC as a function of I (amps) is obtained:

$$V = -6.48 \times 10^{-5} I + 1.267 \tag{13}$$

Now combining Eqs. (12) and (13), we obtain

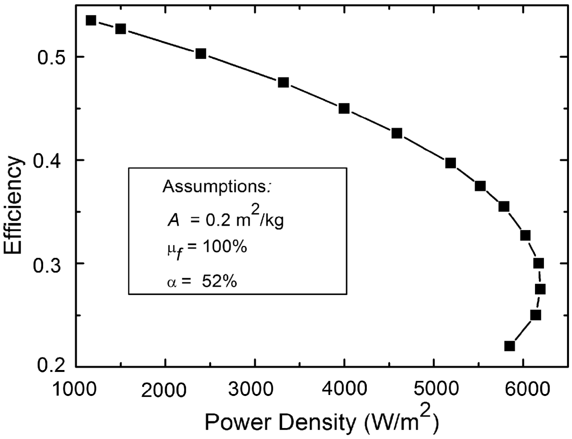

Fig. 3 Peroxide FC efficiency vs power density.

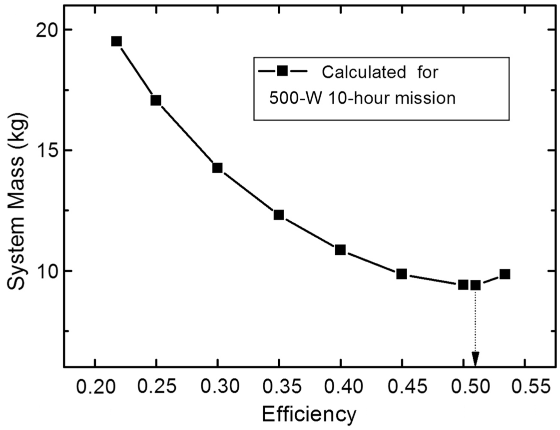

Fig. 4 System mass vs efficiency for a 500-W, 10-h mission.

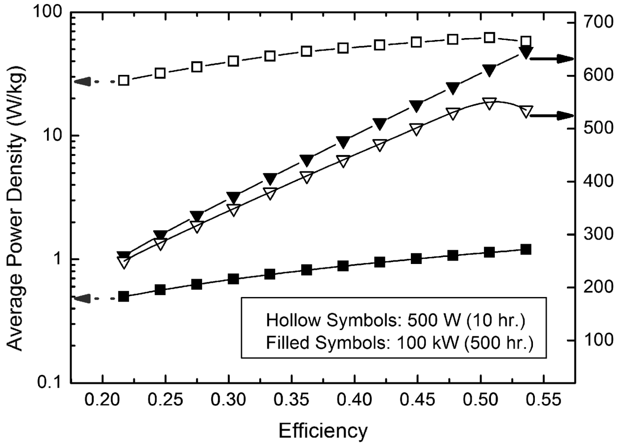

Fig. 5 500-W and 100-kW cell performance. Note that the specific power density calculated here is defined by the specific mission profile. It is averaged over extended mission duration and therefore appears small. It should not be confused with the stack power density which is on the order of 1000 W/kg for peroxide FCs.

$$\rho_P = \frac{-6.48 \times 10^{-5} I + 1.267}{(t_d/1147\mu_f\alpha) + (1/IA)} \tag{14}$$

Based on Eq. (14) a plot of efficiency versus power density of the FC stacks is shown in Fig. 3. As can be seen, the maximum power density of the FC stack occurs at approximately 28% efficiency. On the other hand, the maximum efficiency occurs at increasingly lower power densities. Therefore, improvement in one parameter often is

Table 2 500-W and 100-kW peroxide FC system specifications

Scenario	System mass, kg	Reactant mass, kg	Stack mass, kg	Stack area, m^2	Stored energy, $kW \cdot h$
500 W (10 h)	9.3	8.2	1.1	0.22	5.02
100 kW (10 h) w/500 W nominal operation	2240.0	2020.0	220.0	44.0	1251.0

gained at the expense of the other. Later it shall be shown that the system is optimized at approximately 51% efficiency.

The effect of reactant concentrations, α, on the parameterized FC shall be obvious. Understandably, the higher the reactant concentrations, the better the cell's specific performance. Solution concentrations in the range of 50 to 55% appear to be obtainable at this stage. This range of values assumes an H_2O_2 concentration of 60% combined with the maximum obtainable concentration of $NaBH_4$ of 35.5% at 25°C [26]. With such concentrations, system specific energy densities in the range of 500 to 700 $W \cdot h/kg$ can be obtained. Furthermore, future research into the use of anion exchange membranes as opposed to cation exchange membranes, and the possible use of ammonia as a solubility enhancer, may allow the use of much higher concentration. If sodium borohydride is used as 100% concentration (~solid $NaBH_4$), it would bring the overall reactant concentrations to the range of 65 to 70%, and potentially increase the system specific energy density to values as high as 1000 $kW \cdot h/kg$.

C. 500-Watt and 100-Kilowatt Open-Cycle Peroxide FC

Here the above parameterization is demonstrated for two $NaBH_4/H_2O_2$ FCs. The first one is a 500-W and 10-h-mission-type cell under development for NASA for potential rover applications. The second is single discharge of all of the stored energy during a short lifetime mission characterized by a rapid response launch and 21-day (approximately 500 h) mission. The desired level of output power delivered must be capable of reaching 100 kW.

The FC efficiency versus system mass and efficiency versus specific energy/power density are plotted in Figs. 4 and 5, respectively. Figure 4 shows that the optimal (minimum) system mass to obtain the required power output and mission life is 9.3 kg, corresponding to 51% efficiency. At this point the area power density is 2275 W/m^2. Then with Fig. 5, a specific mission power density of 54 W/kg is obtained. Because the mission duration is 10 h, it can easily be seen that the specific energy density is simply 10 times the specific mission power density, or 540 $W \cdot h/kg$. Note that the relatively high efficiency of 51% is only from 500-W power output, and different power levels will give different optimal efficiencies.

With the mass of the FC established, the energy available is found at 5.02 $kW \cdot h$. We can also find the mass of the FC stacks and the corresponding total cell area. To do this the 500-W output is divided by the stack mass-power density to find a stack mass of 1.10 kg. Next multiplying by the active area per unit mass, an active area of 0.22 m^2 is obtained. Last the mass of the reactant solutions is found by simply subtracting the cell stack mass from the total mass to obtain 8.2 kg. These results are summarized in Table 2.

The 100-kW scenario is slightly more complicated. If it is assumed that the system operates at 100 kW throughout the life of the mission, a system mass of approximately 78,000 kg is found. Such a large system mass makes this an unattractive mission due to the expense. Therefore, for this scenario, it will be assumed that the FC system is only operated at 100 kW for a total duration of 10 h. During the rest of the mission, the system is assumed to operate at a nominal power mode of 500 W. Table 2 summarizes both scenarios and specifically reports system mass, reactant mass, stack mass, stack area, and stored energy. From this table it can easily be seen that the more power and longer mission time required, the larger the system mass/size becomes.

IV. Conclusions

Both experimental and theoretical studies have been performed to investigate the properties and application potential of peroxide-based fuel cells for use in space power systems. Studies of small prototype cells have confirmed the feasibility and excellent performance of the direct, all-liquid, $NaBH_4/H_2O_2$ fuel cell. Such a technology offers many advantages for space applications. A parametric system analysis of hypothetical 500-W and 100-kW units reveals very attractive size and weight characteristic for a variety of demanding space missions. Although studies of higher power units are needed to fully evaluate this approach, the potential of the peroxide-based fuel cell is clearly demonstrated. A next step involves construction of a kW level unit under NASA sponsorship.

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