H$_2$O$_2$-Based Fuel Cells for Space Power Systems

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A new type of fuel cell (FC) using novel fuel and oxidizer is investigated in this research. H$_2$O$_2$ is used in this unique FC directly at the cathode. Two types of reactant, namely a gas-phase hydrogen and an aqueous NaBH$_4$ solution, were utilized as fuel at the anode. The direct utilization of H$_2$O$_2$ and NaBH$_4$ at the electrodes, as seen in experiments, results in >30% higher voltage output compared to the ordinary H$_2$/O$_2$ FC. Further, the unique combination of NaBH$_4$ and H$_2$O$_2$, 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 FC is uniquely suited for space power applications where air is not available and a high energy density fuel is essential.

Nomenclature

\[
\begin{align*}
A & = \text{Active Area per Unit Mass (m}^2/\text{kg)} \\
E_V & = \text{Reversible Open-Circuit Voltage (V)} \\
I & = \text{Discharge Current Density (A/m}^2) \\
M_F & = \text{Mass of Fuel (kg)} \\
M_S & = \text{Mass of FC Stack (kg)} \\
P & = \text{Output Power (W)} \\
T_d & = \text{Discharge Time (hr)} \\
V & = \text{Discharge Voltage (V)} \\
\alpha & = \text{Concentration of Reactants in Solution (\%)} \\
\eta_D & = \text{Discharge Energy Conversion Efficiency (\%)} \\
\eta_e & = \text{Energy Conversion Efficiency (\%)} \\
\mu_f & = \text{Reacted Fuel Coefficient (\%)}
\end{align*}
\]

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Theoretical Energy Output (W⋅hr)
\[ \xi \]

Specific Energy Density (W⋅hr/kg)
\[ \rho_E \]

Fuel Specific Power Density (W/kg)
\[ \rho_F \]

Specific Power Density (W/kg)
\[ \rho_P \]

Stack Specific Power Density (W/kg)
\[ \rho_S \]

I. Introduction

Hydrogen peroxide (H$_2$O$_2$) 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 Messerschmitt ME-163 “Komet” rocket plane. It is also widely utilized for underwater power systems, and has the following desired properties as an energetic material:

**Powerful** - H$_2$O$_2$ is one of the most powerful oxidizers. Through catalysis, H$_2$O$_2$ can be converted into hydroxyl radicals (OH) with reactivity second only to fluorine. By using catalysts such as Fe$^{2+}$, H$_2$O$_2$ can be readily converted into hydroxyl ion (OH$^-$), which makes it a desired reactant for a fuel cell (FC). Combined with different fuels, H$_2$O$_2$ forms a potent rocket propellant. With hydrogen the specific impulse is over 322 seconds in vacuum.

**Safe** - H$_2$O$_2$ is a natural metabolite of many organisms. When decomposed it gives only oxygen and water. H$_2$O$_2$ is also formed by the action of sunlight on water, a purification system of Nature. Consequently, H$_2$O$_2$ has none of the environmental problems associated with many other chemical oxidizers.

**Widely Used** - H$_2$O$_2$ 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$_2$O$_2$ for aerospace power applications, as witnessed by the recent International Hydrogen Peroxide Propulsion Conference. This revival was prompted by environmental concerns and accelerated by the dropping price of H$_2$O$_2$.

The use of hydrogen peroxide in FC’s is a relatively new development, however. The Naval Underwater Weapon Center (NUWC), Swift Enterprises and others have fabricated some semi-FC devices using Al for the anode. Very recently, full fuel cells based on H$_2$/H$_2$O$_2$ and on NaBH$_4$/H$_2$O$_2$ have been investigated at NPL Associates, Inc., the University of Illinois (UIUC) and elsewhere. Studies at Swift Enterprises have shown that bioelectrocatalysts (BEC) can electro-catalyze 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 utilizes air as the oxidizer.
and therefore H$_2$O$_2$ was not studied for applications where air is readily available, such as ground transportation. However, for space or underwater applications, H$_2$O$_2$ based systems (whether heat engine or FC based) are an ideal choice. The reasoning for this will be further delineated in the next section.

A. H$_2$O$_2$ Compared to Other Oxidizers

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$_2$O$_4$. The use of N$_2$O$_4$ 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 one ton of LOX is only on the order of one month, while most satellites today call for a mission duration of several years. Bottled high-pressure oxygen is not an ideal option either because its storage efficiency is rather low (often ~ 0.3 kg/liter).

In comparison, H$_2$O$_2$ 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$_2$O$_2$ 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$_2$O$_2$ solution. Thus, short time overloading or pulsing can be achieved by increasing the H$_2$O$_2$ concentration at the cathode side.

B. Benefits of H$_2$O$_2$ in Fuel Cells

The benefits of a direct H$_2$O$_2$ FC compared to cells utilizing gaseous oxygen are many-fold:

*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 a thousand 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).

*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. 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 H₂O₂ FC largely bypasses these transport problems.

Eliminating the O₂ reduction over-potential 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:

\[ \text{O}_2 + 4 \text{H}^+ + 4 \text{e}^- \rightarrow 2 \text{H}_2\text{O} \]

This reaction involves the simultaneous transfer of four electrons, and therefore has a low probability of occurrence.¹⁷-¹⁸ A high cathodic over-potential loss of 220 mV while operating close to the open circuit voltage has been observed in state-of-the-art Pt loading electro-catalysts. This is due to a mixed potential that is set up at the oxygen electrode. The mixed potential is from a combination of slow O₂-reduction kinetics and competing anodic processes such as Pt-oxide formation.¹⁹-²⁰ It has been determined that the exchange current density of O₂-reduction is 6 orders of magnitude lower than that of H₂-oxidation.²¹ In comparison, the H₂O₂ reduction process at the cathode,

\[ \text{H}_2\text{O}_2 + 2 \text{e}^- \rightarrow 2 \text{OH}^- \]

is a two-electron-transfer process involving a much lower activation barrier. This improvement therefore circumvents the over-potential problem of a H₂/O₂ fuel cell.

II. Experimental Set-up 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 cross-over 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 H₂/O₂ fuel cell mainly in the membrane electrode assembly (MEA). The fabrication of the MEA starts with the catalyst ink. The catalysts used in the UIUC/NPL part of work are mostly of the Pt-type whereas studies at Swift are based on bio-electrocatalysts, such as horseradish peroxidase, microperoxidase-11, and metal-5,10,15,20-tetrakis-(p-methoxyphenyl)porphyrin. The latter has the advantage of negligible peroxide decomposition at a price of reducing current/power density. 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” instead of the often-cited “gas diffusion layer” because most of the peroxyde FC reactants are in liquid phase. The diffusion layer used for the H₂ 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 diffusion electrodes, are then dried out in an oven at 80°C for one hour. The effective loading of the catalyst is maintained at 1 mg/cm² throughout the studies at UIUC and NPL.

A Dupont Nafion 112 membrane is used as the electrolyte. It was boiled in aqueous solution of 3%-wt H₂O₂ + 3%-wt H₂SO₄ for one hour before rinsing in de-ionized (DI) water for two hours. The Nafion PEM is then activated by 0.5M H₂SO₄ for two hours, 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 pound per square inch (psi). This hot-pressing typically last about 30 seconds 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 and a typical finished unit is shown in Fig. 1.
B. Performance of Peroxide FC

Liquid reactants, namely water solutions of NaBH$_4$ and H$_2$O$_2$, were circulated by a Cole-Parmer diaphragm pump, at a flow rate $\sim$ 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$_2$O$_2$ FC. The V-I characteristic curves of both FC’s 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 FC’s are given in Fig. 2 along with those of traditional H$_2$/O$_2$ FC’s for comparison.
Fig. 2 The V-I characteristics of various FC’s at room temperature, and ambient pressure operation. Note the prominent H₂O₂ FC performance. The curve for the H₂/H₂O₂ fuel cell is tested with a pH=2 catholyte.

There are a few of observations worth mentioning. First, both peroxide fuel cells have a higher open circuit voltage than that of a typical H₂/O₂ PEM FC (< 1 V). This is to be expected since both have fairly high thermodynamically reversible open-circuit potential:

\[
\begin{align*}
\text{H}_2 + \text{H}_2\text{O}_2 & \rightarrow 2 \text{H}_2\text{O}, & 1.78 \text{ V} \\
\text{NaBH}_4 + 4 \text{H}_2\text{O}_2 & \rightarrow \text{NaBO}_2 + 6 \text{H}_2\text{O}, & 2.25 \text{ V}
\end{align*}
\]

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 peroxide FC’s, it is not very impressive compared to the theoretical potential. For example, the 1.4 V open-circuit voltage of the NaBH₄/H₂O₂ FC is only 62% of that theoretically achievable. This is likely due to some cross-over 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, which will be addressed in future research.

It is also interesting to compare the current results to those of the Indian Institute of Science (IIS), who have investigated a related cell. Some differences in the two prevent a direct comparison, however. A predominately rare
earth alloy is used in the IIS anode while the UIUC/NPL 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:

\[ E_r (\text{H}_2\text{O}_2) = 1.78 - 0.059 \text{pH} \]

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 UIUC/NPL 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 current density and power density side, the UIUC/NPL results appears several times higher than the IIS results, possibly due to Pt catalysts used in the anode, which are electrochemically more active.

The small peroxide fuel cell prototype reported here can readily drive a watt-level electric motor as evident in Fig. 3. The motor is placed on top of an aluminum box, with a propeller attached to its hub. On the left side, the electrolyzer was turned off so that no hydrogen was generated to feed the FC. Thus, the propeller was at rest. On the right, the FC is now fed with hydrogen, and the propeller starts rotating.

![Fig. 3 A peroxide FC drives an electric motor.](image)

The theoretical potential of the NaBH₄/H₂O₂ electrochemical couple is around a full one volt higher than the standard potential of a H₂/O₂ 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. 2, the peroxide-based FC’s (both H₂/H₂O₂ and NaBH₄/H₂O₂) indeed offer higher voltage and current density than obtained from traditional FC’s at similar conditions.
Experimentally, a power density of 0.6 W/cm² was achieved with the H₂/H₂O₂ FC while the NaBH₄/H₂O₂ FC reached 0.8 W/cm², both at room temperature and ambient pressure. These quoted numbers refer to the UIUC/NPL peroxide fuel cells that use carbon supported platinum catalysts at the electrode. Table 1 lists the best UIUC results achieved. For the Swift peroxide FC using BEC at the cathode, the power density is usually on the order of 1-10 mW/cm².

<table>
<thead>
<tr>
<th>Type</th>
<th>Ideal Energy Density (W·hr/kg)</th>
<th>Voltage (Open circuit)</th>
<th>Current (Short circuit)</th>
<th>Max. power density</th>
<th>Efficiency @ 100 mA/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂/H₂O₂</td>
<td>2728</td>
<td>&gt;1.05 V</td>
<td>&gt;1.8 A/cm²</td>
<td>&gt;0.6 W/cm²</td>
<td>&gt;55%</td>
</tr>
<tr>
<td>NaBH₄/H₂O₂</td>
<td>2580</td>
<td>&gt;1.40 V</td>
<td>&gt;3.0 A/cm²</td>
<td>&gt;0.7 W/cm²</td>
<td>~55%</td>
</tr>
</tbody>
</table>

The experimentally achieved energy density is around 1000 W·hr/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 the dismounted infantry on battlefield could benefit from the high theoretical power densities of the NaBH₄/H₂O₂ fuel cell technology. Batteries currently power a myriad of equipment (sensors, communications, night vision, etc.) that the infantry carries into combat. However, the US Army's Future Force Warrior Program is developing new equipment for the dismounted force. A mean power requirement of 20 W for a 72-hour mission would equate to an energy requirement of 1.44 kW·hr. Current battery technologies (Li/SOCl₂ and Li/MnO₂, for example) involve a weight penalty of approximately 200% to 400% (5.14 kg and 9.94 kg total system weight respectively compared to a hydrogen fueled PEM fuel cell with the hydrogen fuel stored at 5,000 psi (2.09 kg system weight). The associated energy densities equate into 280 W·hr/kg for the Li primary battery, 145 W·hr/kg for the Li/MnO₂ battery, and 1,034 W·hr/kg for a typical PEM system (the PEM system was evaluated at 30W mean output and 2,160 total W·hr). It is generally true that longer mission times and higher energy requirements would favor a fueled system over batteries. Consequently, the NaBH₄/H₂O₂ fuel cell technology described in this paper could be a viable solution for the ever-increasing power requirements of the dismounted infantry, given a three fold higher energy density than the best lithium battery.

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 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 \( \text{H}_2/\text{H}_2\text{O}_2 \) and conventional \( \text{H}_2/\text{O}_2 \) FC’s.

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 \( \text{H}_2 \) and \( \text{O}_2 \), has long been the hurdles limiting the performance of RFC. In a typical \( \text{H}_2/\text{O}_2 \), 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 \( \text{H}_2/\text{O}_2 \) RFC, forcing separate units for these functions. Another issue in unitized design for \( \text{H}_2/\text{O}_2 \) RFCs is the huge over-potential (0.4V) involved in both oxygen reduction and generation. A single material is very difficult to function as both an \( \text{O}_2 \) evolution and reduction electrodes. In contrast, a \( \text{NaBH}_4/\text{H}_2\text{O}_2 \) cell bypasses both problems. Thus, a unitized RFC appears quite feasible for a \( \text{NaBH}_4/\text{H}_2\text{O}_2 \) fuel cell, and initial experiment at that direction are quite encouraging. Indeed, the very first regenerative operation in the UIUC/NPL prototype \( \text{NaBH}_4/\text{H}_2\text{O}_2 \) FC has reached an energy density of 65 W·hr/kg, with enormous potential for future growth. The details of this unitized \( \text{NaBH}_4/\text{H}_2\text{O}_2 \) RFC will be separately discussed in a future publication.

C. Performance Summary

In summary, there are a number of prominent features that distinguish the \( \text{NaBH}_4/\text{H}_2\text{O}_2 \) FC from the \( \text{H}_2/\text{O}_2 \) ones and conventional batteries. From a performance point of view, a space power systems based on an open-cycle \( \text{NaBH}_4/\text{H}_2\text{O}_2 \) FC have the following distinct advantages:

1) Very high energy density (over 2580 W·hr/kg theoretical, over 1000 W·hr/kg achieved experimentally, nearly ten 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 \( \text{H}_2\text{O}_2 \) at the cathode;

3) The ability to overload for a short period of time simply by increasing the concentration of \( \text{H}_2\text{O}_2 \) at the cathode;

4) The potential for a very high efficiency (over 60%) because the use of \( \text{H}_2\text{O}_2 \) overcomes the oxygen over-potential problem inherent to prior \( \text{H}_2/\text{O}_2 \) 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·hr/kg proved, and potentially 125–200 W·hr/kg; both nominal and on orbit;

2) Much improved low Earth orbit (LEO) and medium Earth orbit (MEO) cycle performance; 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 NaBH₄/H₂O₂ 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 system. 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. The United Technologies (UTC) Alkaline FC’s 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·hr/kg. Utilizing the non-regenerative NaBH₄/H₂O₂ 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 Ref. 22, 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 $\rho_p$:

$$\rho_p = \frac{P}{M_F + M_S} \quad (1)$$

Then, the specific energy density $\rho_E$ is given by:

$$\rho_E = \rho_p t_d \quad (2)$$

where $t_d$ is the fuel cell discharge time.

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

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

The fuel specific power density can also be characterized by:

$$\rho_F = \frac{E}{t_d M_F} \quad (4)$$

where $E$ is the total energy output.

Rewriting Eq. (4), in terms of the energy conversion efficiency, $\eta_e$, we obtain:
\[
\rho_F = \frac{\eta_c \xi}{t_d M_F}
\]  

(5)

where \(\xi\) is the theoretical energy output while \(\eta_c\) denotes energy conversion efficiency.

The theoretical energy output for hydrogen peroxide/sodium borohydride is 2580 W·hr per 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 \(\alpha\) is now introduced, which represents the percent concentration of the reactants in solution.

Equation (5) can now be rewritten as:

\[
\rho_F = \frac{2580 \eta_c \alpha}{t_d}
\]  

(6)

Since only open-cycle fuel cells are being considered here, \(\eta_c\) is equal to the discharge energy conversion efficiency \(\eta_D\), or

\[
\eta_c = \eta_D
\]  

(7)

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

\[
\eta_D = \mu_f \frac{V}{E_v}
\]  

(8)

where \(V\) is discharge voltage (V) and \(E_v\) represents the reversible open-circuit voltage (OCV) (V).

By using the OCV for NaBH₄/H₂O₂ FC of 2.25V, Eq. (8) can be rewritten as:

\[
\eta_D = \frac{V \mu_f}{2.25}
\]  

(9)

Thus, combining equations (6), (7) and (9) gives:
\[ \rho_F = \frac{1147 V \mu_f \alpha}{I_d} \]  

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

\[ \rho_S = V I A \]  

(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\textsubscript{2}O\textsubscript{2} fuel cells as follows.

**B. Open-Cycle Peroxide Fuel Cells**

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

\[ \rho_p = \frac{V}{\left( \frac{I_d}{1147 \mu_f \alpha} \right) + \left( \frac{1}{I A} \right)} \]  

(12)

Now, to evaluate Eq. (12) the relationship between voltage (V) and current (I) obtained from experimental data in Fig. 4 will be used. Also shown in Fig. 4 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\textsuperscript{2}. Below this range, less than 1000 A/m\textsuperscript{2}, the power density is too low, forcing the FC stack to increase in size, causing the system mass to increase. Above this range (> 12000 A/m\textsuperscript{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:

\[ V = -6.48 \times 10^{-5} I + 1.267 \]  

(13)

Now combining equations (12) and (13), we obtain:

\[ P_p = \frac{-6.48 \times 10^{-5} I + 1.267}{(t_d / 1147 \mu \alpha) + (1/IA)} \]  

(14)

Based on Eq. (14) a plot of efficiency versus power density of the FC stacks is shown in Fig. 5. 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 gained at the expense of the other. Later it shall be shown that the system is optimized at approximately 51% efficiency.
Next the effect of reactant concentrations, $\alpha$, on the parameterized FC shall be considered. Fig. 6 is a plot of efficiency vs. specific energy density for varying concentration of reactant. Apparently, the higher the reactant concentrations are, the better the cell’s specific performance. Solution concentrations in the range of 50 to 55% appear to be obtainable. This range of values assumes an $\text{H}_2\text{O}_2$ concentration of 60% combined with the maximum obtainable concentration of $\text{NaBH}_4$ of 35.5% at 25°C. With such concentrations, system specific energy densities in the range of 500 to 700 W·hr/kg can be obtained. Furthermore, future research into the use of anion exchange membranes as opposed to cation exchange membranes, may allow use of nearly 100 percent sodium borohydride concentration (~ solid NaBH₄). This would bring the overall reactant concentrations to the range of 65 to 70 percent, and potentially increase the system specific energy density to values as high as 1000 kW·hr/kg.
C. 500-W and 100-kW Open-Cycle Peroxide FC

Here the above parameterization is demonstrated for two NaBH₄/H₂O₂ FC’s. The first one is a 500-W and 10-hour-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 hour) 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. 7 and 8, respectively. Fig. 7 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 2,275 W/m². Then with Fig. 8, a specific mission power density of 54 W/kg is obtained. Since the mission duration is 10 hours, it can easily be seen that the specific energy density is simply ten times the specific mission power density, or 540 W·hr/kg.
With the mass of the FC established, the energy available is found at 5.02 kW·hr. 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.
Fig. 8 500-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 FC’s.

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 ten hours. 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.

<table>
<thead>
<tr>
<th>Scenario</th>
<th>System Mass (kg)</th>
<th>Reactant Mass (kg)</th>
<th>Stack Mass (kg)</th>
<th>Stack Area (m²)</th>
<th>Stored Energy (kW-hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500 W (10 hr)</td>
<td>9.3</td>
<td>8.2</td>
<td>1.1</td>
<td>0.22</td>
<td>5.02</td>
</tr>
<tr>
<td>100 kW (10 hr) w/ 500 W nominal operation</td>
<td>2240</td>
<td>2020</td>
<td>220</td>
<td>44.0</td>
<td>1251</td>
</tr>
</tbody>
</table>
IV. Conclusion

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, NaBH₄/H₂O₂ 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. While 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. A commercial version of these peroxide fuel cells is being developed separately at NPL, under the trademark I-Charger™.

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References


