H_2O_2 Based Fuel Cells for Space Power Systems

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Introduction

Desired Properties of H_2O_2

- **Powerful**

H_2O_2 is one of the most powerful oxidizers. 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 seconds in vacuum.

- **Safe**

H_2O_2 is a natural metabolite of many organisms. When decomposed it gives only oxygen and water. H_2O_2 is also formed by the action of sunlight on water, a purification system of Nature.

- **Widely Used**

H_2O_2 is now produced at over a billion pounds per year. The high volume production results in very low cost.

The use of hydrogen peroxide in FC's is a relatively new development, We have done a lot of study on it and got some results. All our results have shown the general feasibility of a peroxide based electrochemical cell. A typical FC utilizes air as the oxidizer and therefore H_2O_2 was not studied for applications where air is readily available, such as ground transportation For space or underwater applications, H_2O_2 based systems (whether heat engine or FC based) are an ideal choice.

Reasons ?

A,B

A . H_2O_2 Compared to Other Oxidizers

Liquid oxygen (LOX)

- LOX is used as rocket propellants. It is environmentally sound, but is not suitable for long-time storage due to its vaporization.

N_2O_4

- The use of N_2O_4 in a FC should be very restricted because of it extreme toxicity.

Bottled high-pressure oxygen

- Its storage efficiency is rather low (often ~ 0.3 kg/liter).

H_2O_2

- storable
- biologically sound and environmentally compatible
- high energy density of concentrated H_2O_2
- 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.

B. Benefits of H_2O_2 in Fuel Cells

- ***Higher current density from larger oxidizer mass density***

  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***

  Two-phase mass transport of reactant is the limiting phenomenon of traditional FC operation. And 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 over-potential problem***

  The oxygen reduction reaction at the cathode is written as:

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

  This reaction involves the simultaneous transfer of four electrons, therefore has a low probability of occurrence.

  In comparison, the H_2O_2 reduction process at the cathode,

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

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

Experimental Set-up and Results

A. Fabrication of the Peroxide Fuel Cell

MEA

-nafion 112 membrane is used as the electrolyte.

-carbon supported Pt catalyst

-reactant diffusion layer

Perforated stainless steel plates

Bolts, Nuts

Two polycarbonate end plates

Liquid-tight seal (silicone elastomer)

Fig. 1

The prototype H_2/H_2O_2 FC outperforms an ordinary H_2/O_2 FC at room temperature and ambient pressure.

B. Performance of Peroxide FC

Liquid reactants : 20%-wt $NaBH_4$ stabilized with 1.8 M potassium hydroxide (KOH)

20%-wt H_2O_2 stabilized with 5%-wt phosphoric acid

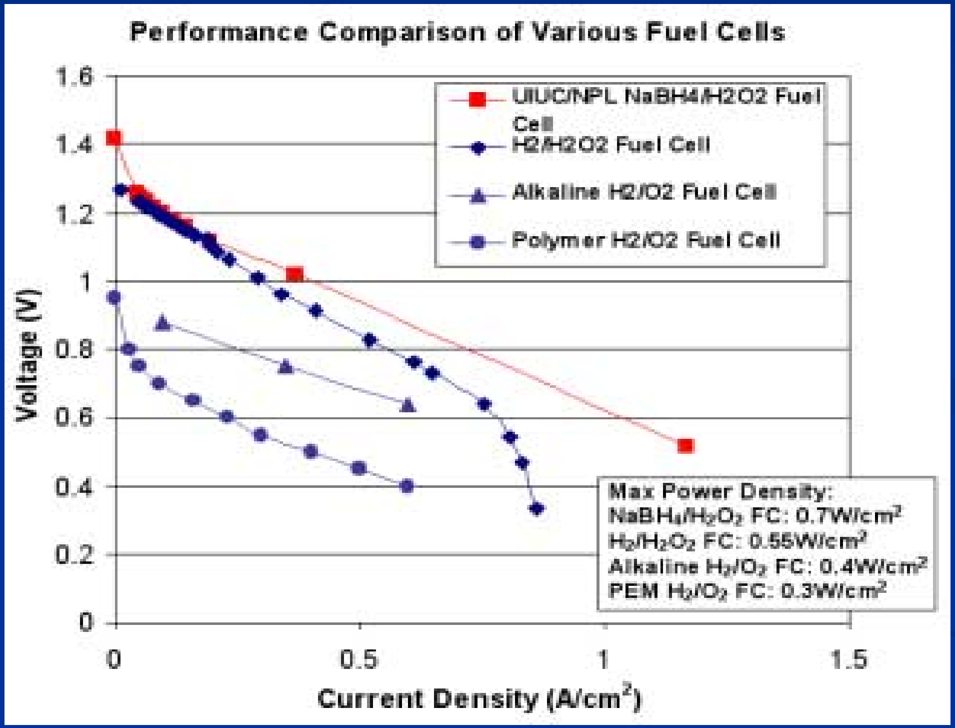

Fig. 2

The V-I characteristics of various FC's 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.

Observations

- Both peroxide fuel cells have a higher open circuit voltage than that of a typical H_2/O_2 PEM FC (< 1 V)

- 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.

- 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 $NaBH_4/H_2O_2$ FC is only 62% of that theoretically achievable.

- The small peroxide fuel cell prototype can readily drive a watt-level electric motor

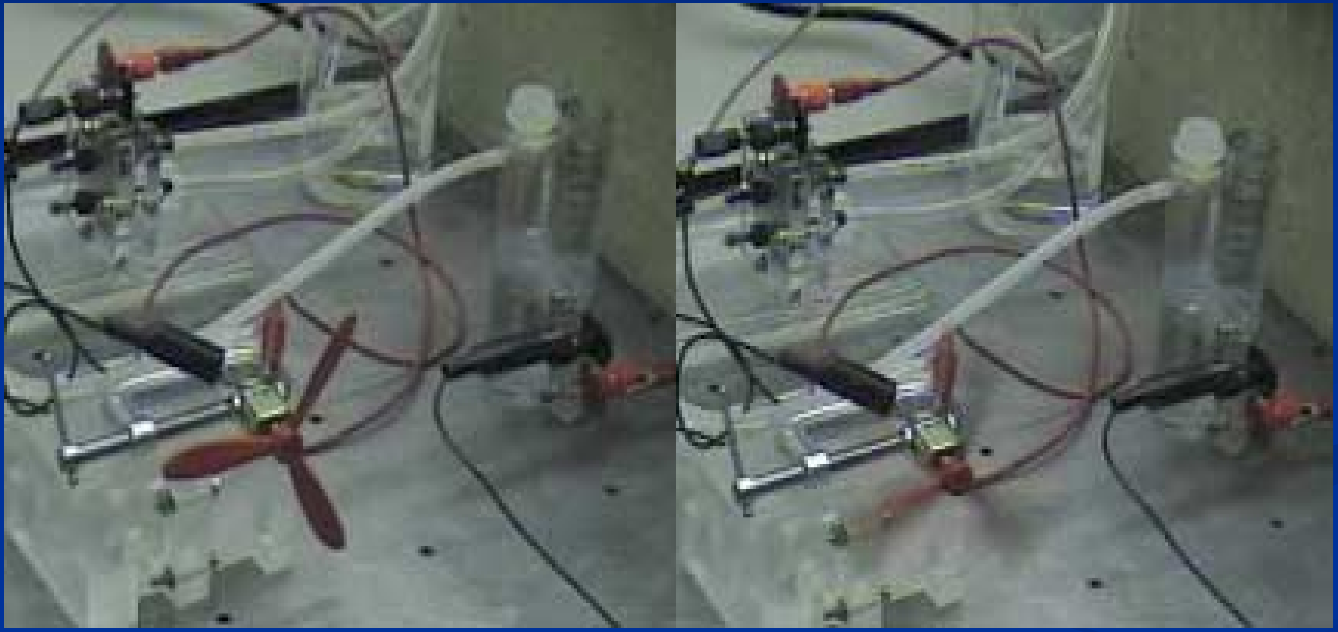

Fig. 3 a peroxide FC drives an electric motor.

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.

- Power density of ***0.6 W/cm²*** was achieved with the H_2/H_2O_2 FC while the $NaBH_4/H_2O_2$ FC reached ***0.8 W/cm²***, both at room temperature and ambient pressure

Table 1 Performance of UIUC/NPL peroxide FC's at 1 atm. and 300K

Type	Ideal Energy Density (W·hr/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%

- 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

- 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*.

1. No water humidifier is needed because the Nafion PEM is 100% saturated with water

2. The liquid reactant offers a fairly large heat removal capacity so that separate liquid cooling loop is not needed

- A unitized **RFC(regenerative fuel cell)** appears quite feasible for a $NaBH_4/H_2O_2$ fuel cell, and initial experiment at that direction are quite encouraging. Indeed, the very first regenerative operation in the UIUC/NPL prototype $NaBH_4/H_2O_2$ FC has reached an energy density of ***65 W·hr/kg***, with enormous potential for future growth.

C. Performance Summary

From a performance point of view

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 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 over-potential problem inherent to prior H_2/O_2 FC designs

For the regenerative (closed-cycle) operation

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

1) Environmentally safe
2) Long-time storage of energetic materials
3) Low operational cost

Operation scenarios for novel space power system

A. Space-borne directed energy beam systems

This kind of system requires a peak power level of 100 kW, 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. The Space Shuttle power system is a good example.

B. Powering a rover on the lunar surface

The Apollo type rovers had electric motors totaling about 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 $NaBH_4/H_2O_2$ FC could readily extend the rover mission range by a factor of 5-10.

Performance Study of Peroxide FC Applications

A. Generalized Parameterization

$$\rho_P = \frac{P}{M_F + M_S} = \frac{1}{(1/\rho_F) + (1/\rho_S)}$$

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

$$\rho_S = VIA$$

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

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

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

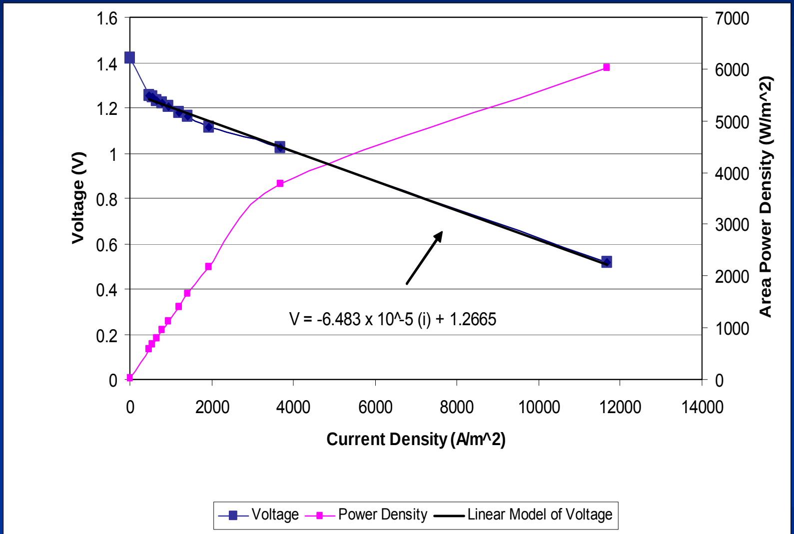

Fig. 4

Experimental performance of the UIUC/NPL NaBH4/H2O2 FC and a linear fit.

A = Active Area per Unit Mass (m^2/kg)
Ev = 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 (hr)
V = Discharge Voltage (V)
= Concentration of Reactants in Solution (%)
= Discharge Energy Conversion Efficiency (%)
= Energy Conversion Efficiency (%)
= Reacted Fuel Coefficient (%)

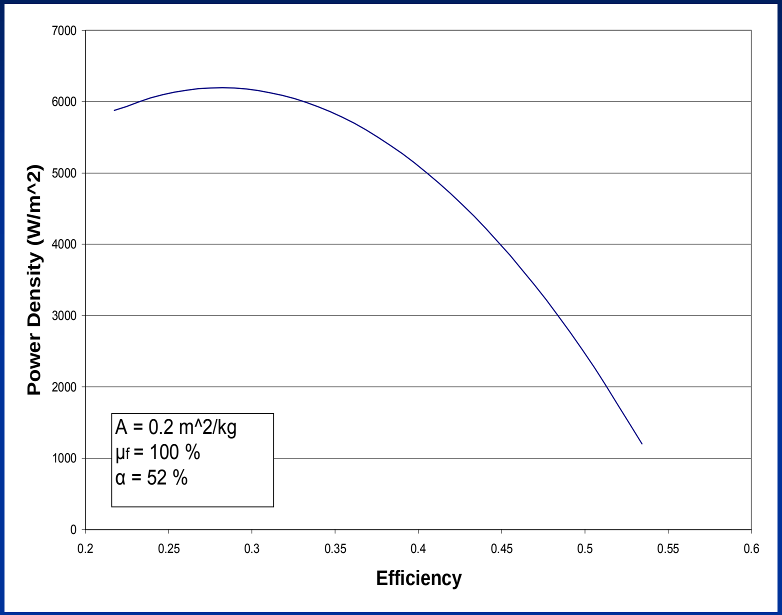

Fig. 5
Peroxide FC efficiency vs. power density

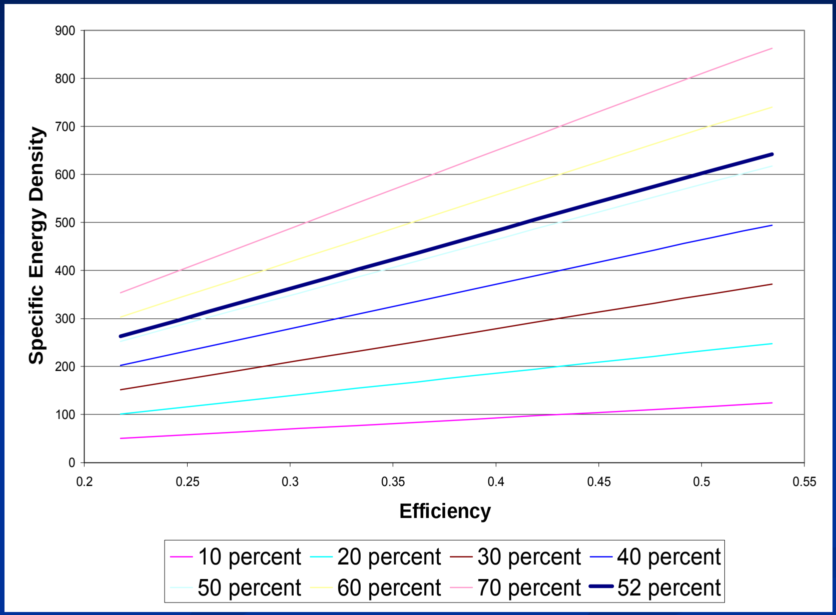

Fig. 6
Efficiency vs. specific energy density for varying α

As can be seen, the maximum power density of the FC stack occurs at approximately 28% efficiency.

the higher the reactant concentrations are, the better the cell's specific performance.

B. 500-W and 100-kW Open-Cycle Peroxide FC

500-W(10 hour) ------ under development for NASA for potential rover applications

100-KW(500 hour)----- single discharge of all of the stored energy during a short lifetime mission

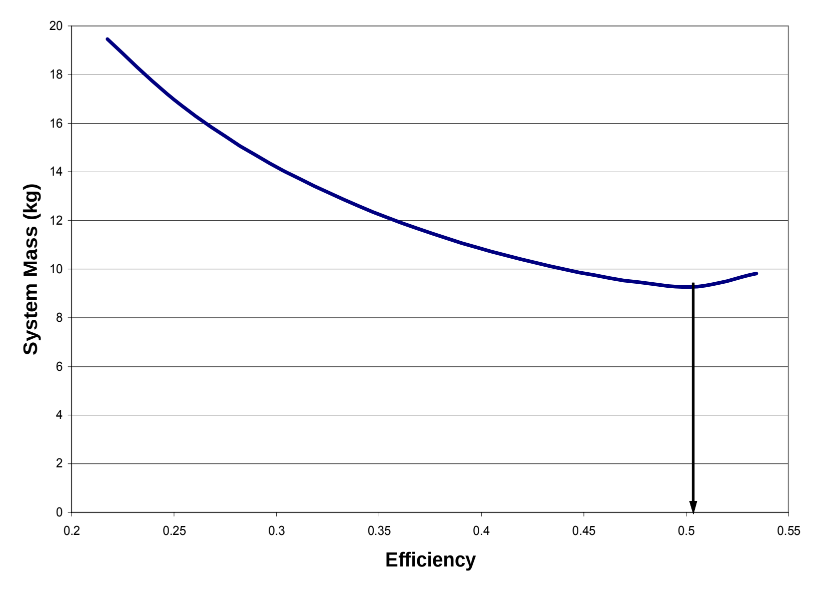

Fig. 7 System mass vs. efficiency for 500-W, 10-hr mission

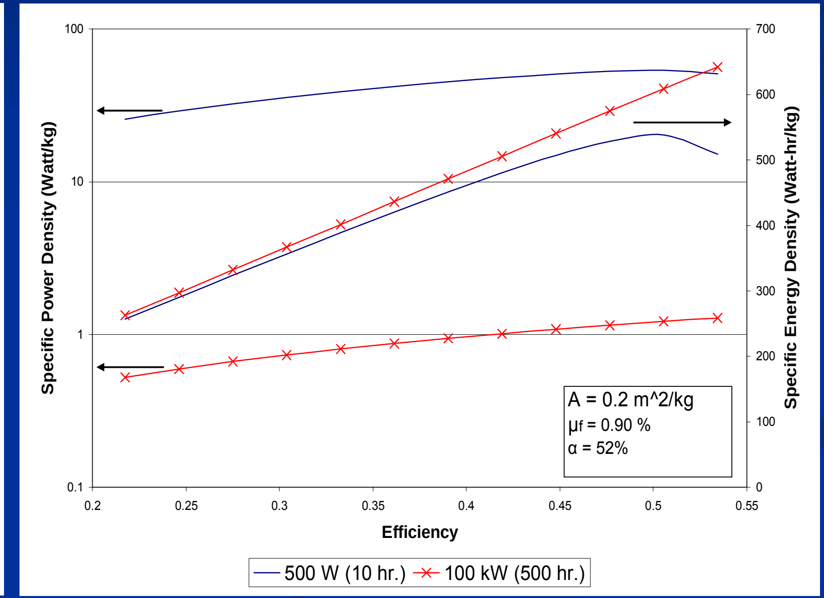

Fig. 8 500-W and 100-kW cell performance. Note that the specific power density calculated here is defined by the specific mission profile. It is averaged over extended mission duration and therefore appears small. It should not be confused with the stack power density which is on the order of 1000 W/kg for peroxide FC's.

the 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/m^2

specific mission power density of 54 W/kg is obtained

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 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·hr)*
500 W (10 hr)	9.3	8.2	1.1	0.22	5.02
100 kW (10 hr) w/ 500 W nominal operation	2240	2020	220	44.0	1251

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, $NaBH_4/H_2O_2$ fuel cell. Such a technology offers many advantages for space applications.

- 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.

- 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™**.

Thank you !

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