

## A high performance hydrogen/chlorine fuel cell for space power applications

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### Abstract

This article discusses the proton-exchange membrane fuel cell (PEMFC) as a high power and energy density power source. The two systems  $H_2/Cl_2$  and  $H_2/O_2$  PEMFC systems were compared over a wide range of mission lifetimes. It has been shown that the development of a  $H_2/Cl_2$  PEMFC could yield a system with power and energy densities inherently greater than currently available in  $H_2/O_2$  PEMFC.

### Introduction

NASA has numerous airborne/spaceborne applications for which high power and energy density power sources are needed. The proton-exchange membrane fuel cell (PEMFC) is an attractive candidate for such a power source. PEMFCs offer many advantages for airborne/spaceborne applications. They have high power and energy densities, convert fuel to electrical power with high efficiency at both part and full load, and can rapidly start up and shut down. In addition, PEMFCs are lightweight and operate silently.

A significant impediment to the attainment of very high power and energy densities by PEMFCs is their current exclusive reliance on oxygen as the oxidant. Conventional PEMFCs oxidize hydrogen at the anode and reduce oxygen at the cathode. The electrode kinetics of oxygen reduction are known to be highly irreversible, incurring large overpotential losses. In addition, the modest open-circuit potential of 1.2 V for the  $H_2/O_2$  fuel cell is unattainable due to mixed potential effects at the oxygen electrode. Because of the high overpotential losses, cells using hydrogen and oxygen are capable of achieving high current densities only at very low cell voltages, greatly curtailing their power output. Based on experiment work at PSI Technology Company (PSIT) on chlorine reduction in a gas diffusion electrode, we believe significant increases in both the energy and power densities of PEMFC systems can be achieved by employing chlorine as an alternative oxidant.

### Background

A hydrogen/chlorine fuel cell reacts hydrogen and chlorine to form hydrogen chloride, A schematic of a proposed system is shown in Fig. 1. Hydrogen gas is oxidized at

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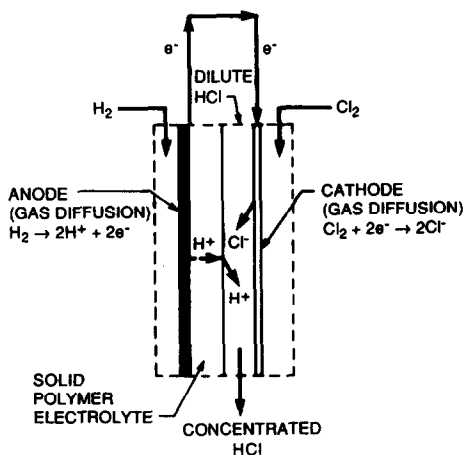


Fig. 1. Schematic of  $\text{H}_2/\text{Cl}_2$  fuel cell using a gas diffusion chlorine electrode with a flowing electrolyte. A captive electrolyte system for short-term applications is also an option.

the anode to produce protons which are transported across the cation-exchange membrane. Chlorine gas is reduced at the cathode to produce chloride ions. Depending on the application duty cycle and lifetime requirements either a captive or flowing electrolyte may be used.

The net cell reaction is  $\frac{1}{2}\text{H}_2 + \frac{1}{2}\text{Cl}_2 \rightarrow \text{HCl}$ . The standard cell potential for this reaction is 1.36 V at 25 °C. In an actual fuel cell the operating voltage is lower due to polarization and ohmic losses. Consequently, the power output is lower than the theoretical power output. Nonetheless, both the oxidation of hydrogen and the reduction of chlorine are known to be relatively nonpolarizable electrochemical reactions and capable of high cell voltages at high current densities.

We can support this statement for chlorine reduction with our own measurements using the rotating disc electrode (RDE) technique [1] to determine mass-transport parameters and mass-transport corrected kinetic and mechanistic information about chlorine reduction. We have used the RDE technique to obtain the exchange current density for chlorine reduction on platinum in 7 M HCl at 25 °C [2] from a mass-transport corrected Tafel plot. We calculated an exchange current density of about  $10^{-1}$  mA/cm<sup>2</sup>. This value is approximately eight orders of magnitude greater than the exchange current density for oxygen reduction on platinum ( $10^{-9}$  mA/cm<sup>2</sup>).

Relatively little research has been reported on  $\text{H}_2/\text{Cl}_2$  fuel cells. Recent research has focused on  $\text{H}_2/\text{Cl}_2$  regenerative fuel cells for load-leveling applications [3–7]. The regenerative fuel cell application, although related, is quite different from the  $\text{H}_2/\text{Cl}_2$  fuel cell discussed here. In the regenerative fuel cell the chlorine electrode acts in both the consuming (cathodic) and generating (anodic) modes, while the system referred to in this paper needs to be optimized for the chlorine consuming mode only.

In the  $\text{H}_2/\text{Cl}_2$  regenerative fuel cell, the hydrogen catalyst is attached to a Nafion™ cation-exchange membrane to prevent chloride ion from poisoning the platinum electrocatalyst. Halide ions, in general, and chloride, in particular, have been shown to alter the adsorption isotherms of hydrogen on platinum [8, 9]. The chlorine reactant is dissolved in the electrolyte and is oxidized at a flow-by electrode during the electrolysis (charge) mode and is reduced at a flow-by electrode during the fuel cell (discharge)

mode. However, mass-transport limitations at the flow-by electrode decrease the cathode performance and limit the power output during discharge.

For a  $H_2/Cl_2$  fuel cell for NASA, we suggest the use of gas diffusion electrodes analogous to those used in  $H_2/O_2$  proton-exchange membrane fuel cells for power generation. Besides the PSIT work reported in this paper, there is only one report of the use of a chlorine-consuming gas diffusion electrode [10], for the chlorination of various organics. However, due to limitations of the organic anode reaction, performance at the chlorine gas diffusion electrode could not be abstracted. Even so, the mass-transport limitations at a chlorine gas diffusion electrode should be considerably less than at flow-by or flow-through electrodes [11].

## Research at PSIT

PSIT is developing  $H_2/Cl_2$  fuel cells for application to chlor-alkali technology. These fuel cells are intended for widespread commercial use, hence, capital cost considerations are paramount. Furthermore, high current densities are neither anticipated nor required. Consequently, our current efforts are concerned with developing low-cost, low-loading electrocatalysts.

Under a Phase II SBIR Program of the US Department of Energy, PSIT developed a  $H_2/Cl_2$  fuel cell technology to reduce the power requirements and increase the system efficiency of brine electrolysis in the chlor-alkali industry. In this program, PSIT determined: (i) the kinetics of chlorine reduction on several catalysts; (ii) the actual polarization behavior of a chlorine gas diffusion electrode; (iii) the conductivity of a commercially available membrane in the environment of interest to our system, and (iv) the conductivity of HCl as a function of concentration. Using these data, we projected very favorable polarization behavior for our  $H_2/Cl_2$  fuel cell. In addition, we engaged in chlorine gas diffusion electrode development and constructed a laboratory-scale process development unit (PDU) for the  $H_2/Cl_2$  fuel cell.

The subject of this paper differs from that of our current developmental efforts in the need to develop electrodes and fuel cells capable of very high current densities at moderate voltages. The NASA application requires much higher performance electrodes. PSIT is highly familiar with the basic design issues and believes in the feasibility of employing high-loading chlorine and chloride-tolerant hydrogen electrodes capable of high current densities with low overpotential losses. Next, we will summarize our efforts in the areas of chlorine gas diffusion electrode development and chloride-tolerant electrodes for hydrogen oxidation.

We have measured current-potential curves for chlorine reduction at 23 °C in 3 M HCl on a number of different electrocatalysts in a gas diffusion electrode configuration. These electrocatalysts included: (i) high surface area (HSA) carbon black (Ketjen EC300J, AKZO Chemie); (ii) heat-treated HSA carbon black (graphitized Ketjen); (iii) low-loading ( $0.5 \text{ mg Pt/cm}^2$ ) carbon-supported platinum, and (iv) HSA lead-ruthenium mixed metal oxide. The polarization behavior of these materials is shown in Fig. 2. The best chlorine reduction performance was observed for the supported platinum electrocatalyst. These results indicate extremely low polarization behavior ( $70 \text{ mV}$  at  $1 \text{ A/cm}^2$ ) for the supported platinum electrode compared with that of oxygen, which does not even register a current under similar conditions. The measured rest potential of  $1.29 \text{ V}$  shows a mixed potential loss of only  $70 \text{ mV}$  from the equilibrium value of  $1.36 \text{ V}$ , a loss that is also much smaller than that suffered by oxygen electrodes. These results are obtained on what is almost certainly a far from optimal electrode

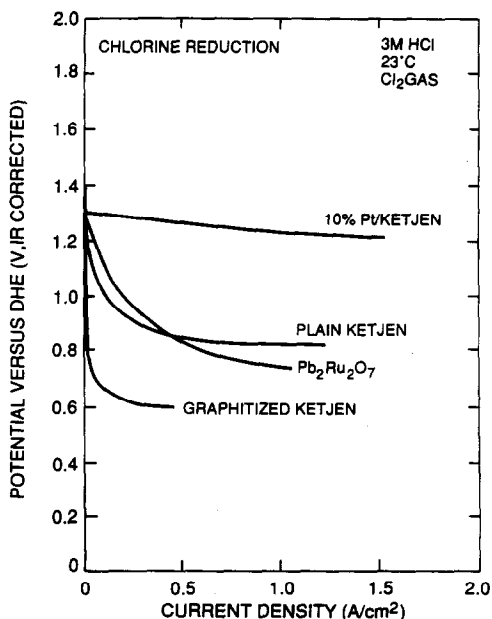


Fig. 2. Chlorine-reduction polarization data in 3 M HCl at 23 °C with (a) 10% platinum/Ketjen; (b) plain Ketjen (c) graphitized Ketjen, and (d) lead-ruthenium oxide. Maximum current density here is determined by IR drop of the half-cell, not by electrode behavior.

structure and are highly encouraging. They form the basis for the conservative power and energy density estimates discussed below.

Chloride ions poison platinum, greatly reducing its effectiveness as an electrocatalyst for hydrogen oxidation. If unchecked, chloride ion poisoning could preclude the attainment of high power and energy densities in the H<sub>2</sub>/Cl<sub>2</sub> fuel cell. In work at PSIT, we have demonstrated that smooth platinum's tolerance of chloride ion was improved by coating the platinum with a thin film of Nafion. Recently, we developed a method to impregnate a carbon-supported platinum gas-diffusion electrode structure with Nafion and coat the individual platinum particles in order to utilize the Nafion's ability to protect platinum from the chloride ion. The method involves soaking the electrode in a Nafion solution for different times to vary the loading of Nafion in the electrode. In Fig. 3, we present the results of electrochemical platinum surface area measurements on electrodes treated with Nafion for 30 s and 12 h. These are compared with results for untreated electrodes that were presoaked in a water/alcohol solution for 30 s and 12 h, respectively, to facilitate wetting upon immersion in the chloride test solutions.

No effect of chloride was seen with any electrode until the 0.1 M chloride concentration. At this value, the standard anode presoaked for 12 h suffered a 47% reduction in surface area, from 112 to 59 m<sup>2</sup>/g. The comparable Nafion-coated anode demonstrated no loss of surface area at the same concentration. The coating of the anode with Nafion, therefore, had a positive effect on the chloride tolerance. The other electrodes also showed no effect at this concentration. The surface area of the lightly coated anode approached that of the heavily coated anode, suggesting improved chloride tolerance for the lightly coated anode as well. Any effect of chloride at 0.1 M on the

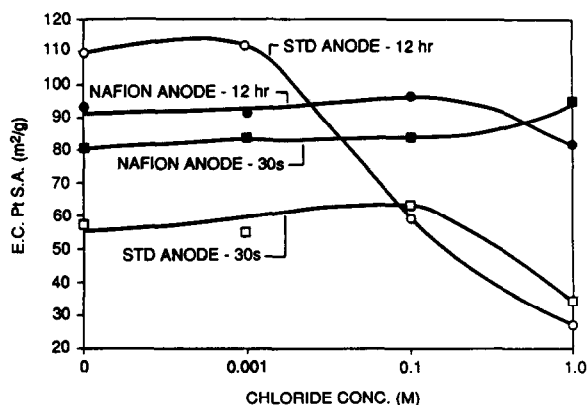


Fig. 3. Results of chloride tolerance study of uncoated and Nafion-coated standard platinum anodes.

untreated anode presoaked for 30 s was probably lost due to incomplete wetting of the electrode.

At 1 M chloride ion concentration, the surface area of both untreated anodes decreased, while the Nafion-coated anodes exhibited little change. This behavior in 1 M HCl clearly demonstrated successful protection of the platinum by coating with Nafion. The total surface area lost for the coated anode was less than 15% compared with a loss of surface area for the uncoated anode of greater than 75%.

### H<sub>2</sub>/Cl<sub>2</sub> PEMFC system performance

To examine the relative merits of the H<sub>2</sub>/Cl<sub>2</sub> PEMFC system compared with the H<sub>2</sub>/O<sub>2</sub> PEMFC system, we estimated the power and energy densities of these two systems over a wide range of mission lifetimes. The results shown in Fig. 4 indicate that the H<sub>2</sub>/Cl<sub>2</sub> PEMFC will significantly outperform the H<sub>2</sub>/O<sub>2</sub> PEMFC. For mission lifetimes of 1 min, 1 h, and 10 h, we conservatively estimate the energy and power densities of the H<sub>2</sub>/Cl<sub>2</sub> PEMFC system to be, respectively, 20 Wh/kg and 1200 W/kg at 0.73 V, 152 Wh/kg and 152 W/kg at 1.12 V and 199 Wh/kg and 20 W/kg at 1.26 V. These values are, respectively, 2, 1.5, and 1.33 times greater than the corresponding values optimistically estimated for an H<sub>2</sub>/O<sub>2</sub> PEMFC system based on state-of-the-art performance recently reported by Watkins *et al.* [12] of the Ballard Power Systems (BPS). For lifetimes greater than 10 h, the energy and power densities of the H<sub>2</sub>/Cl<sub>2</sub> system asymptotically approach 1.3 times those of the H<sub>2</sub>/O<sub>2</sub> system. It is significant that, according to Appleby [13], the energy density figure of 152 Wh/kg (and greater) for the 1-h mission (or longer) 'exceeds the energy available from any known secondary battery, including sodium-sulfur'. Also note that the energy density of the H<sub>2</sub>/Cl<sub>2</sub> system exceeds 110 Wh/kg (50 Wh/lb) for all mission lifetimes longer than 15 min.

The estimates shown in Fig. 4 are based on the following assumptions. The fuel cell stack contains 50 cells of 232 cm<sup>2</sup> (0.25 ft<sup>2</sup>) each and weights 45 kg as suggested by BPS [12]. The assumed mass significantly affects the estimates only for mission lifetimes less than 1 h; for longer missions the mass reactants and storage tanks predominates. The latter masses were taken from an Air Products catalog and are 0.112 kg/mol for chlorine, 0.190 kg/mol for oxygen, and 0.206 kg/mol for hydrogen.

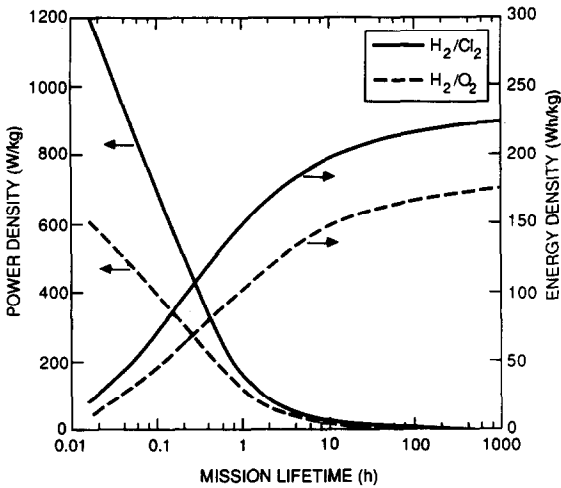


Fig. 4. Estimated optimum power and energy densities vs. mission lifetime for PEMFC systems.

With these assumptions, the mass to power ratio  $M$  (kg/kW) for each system can be written as:

$$M(\text{H}_2/\text{Cl}_2) = 45/P + 5.93t/V \quad (1)$$

$$M(\text{H}_2/\text{O}_2) = 45/P + 5.62t/V \quad (2)$$

where  $t$  is the mission lifetime in hours,  $V$  is the cell potential in V, and  $P$  is the stack power in kW.

The current ( $I$ )–potential ( $V$ ) behavior of a single cell is adequately represented by a linear relation:  $V = V^0(1 - 0.5I/I_p)$ , where  $V^0$  is the rest potential and  $I_p$  is the current at which the peak cell power is obtained. For the BPS  $\text{H}_2/\text{O}_2$  cell at 102 °C and 5.8 atm,  $V^0$  is 0.985 V and  $I_p$  is 1250 A. With these measured values, the linear current–potential relation actually overpredicts cell performance and thus provides optimistic power estimates for the  $\text{H}_2/\text{O}_2$  system. For the  $\text{H}_2/\text{Cl}_2$  cell, we have  $V^0 = 1.34$  V (our measured room temperature value of 1.29 V plus 50 mV Nernst gain for operating at 6 atm) and a projected value for  $I_p$  of 1943 A based on 80 mV loss at 232 A (we measured 70 mV at 1 A/cm<sup>2</sup>). Since this initial chlorine electrode is unlikely to be optimal, these performance predictions should be conservative. Operation at higher temperature with an improved chlorine electrode is certain to give better performance.

It is important to note that since the mass of reactants and storage tanks increases with length of mission, the optimal power and energy densities for a given mission lifetime will occur at a lower current and higher potential than those at the peak power point for the cell. In Fig. 5, the optimum cell potential and total stack power are plotted versus mission lifetime. It is noteworthy that for each mission lifetime, the  $\text{H}_2/\text{Cl}_2$  system achieves optimal power and energy density at a voltage higher than that of the  $\text{H}_2/\text{O}_2$  system. Since the kg/kW due to the reactants and storage tanks varies inversely with the voltage, the advantage of having an electrochemical system with an intrinsically and significantly higher potential at each current is very apparent.

The significantly larger power and energy densities of the  $\text{H}_2/\text{Cl}_2$  system are the result of its larger open-circuit potential and chlorine-reduction kinetics that are

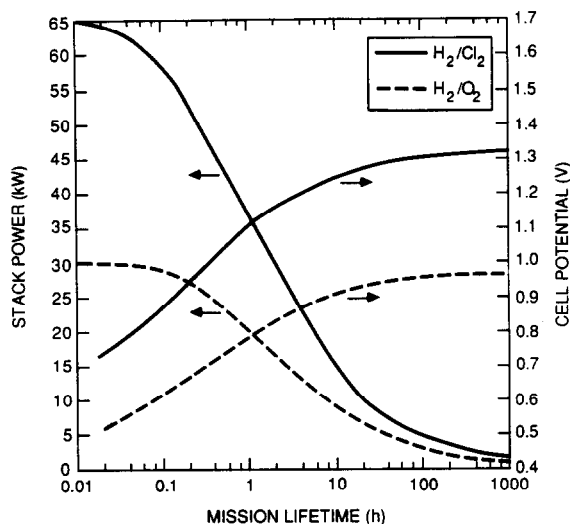


Fig. 5. Estimated optimum cell voltage and stack power vs. mission lifetimes for PEMFC system.

much more reversible than those of oxygen. The theoretical open-circuit potential of a H<sub>2</sub>/Cl<sub>2</sub> cell is about 160 mV higher than that H<sub>2</sub>/O<sub>2</sub>. Moreover, our rest potential measurements indicate a mixed potential loss of only 70 mV, much smaller than for oxygen. Both of these factors combine to provide significantly higher cell voltages. Furthermore, the exchange current density for chlorine reduction on smooth platinum is about eight orders of magnitude greater than that of oxygen, and our measurements show much smaller overpotential losses at high current densities for chlorine than for oxygen. A H<sub>2</sub>/Cl<sub>2</sub> PEMFC therefore appears capable of achieving very high power and energy densities thereby overcoming a severe limitation of oxygen-based cells. Finally, the extremely rapid hydrogen-oxidation and chlorine-reduction kinetics combined with the large freezing point depressions of concentrated HCl should give the H<sub>2</sub>/Cl<sub>2</sub> PEMFC significant cold-start capability.

## Conclusions

The H<sub>2</sub>/Cl<sub>2</sub> PEM fuel cell has the potential to be a versatile and reliable high performance power source for NASA applications. We have shown that the development of a H<sub>2</sub>/Cl<sub>2</sub> PEM fuel cell could yield a system with power and energy densities inherently greater than currently available in H<sub>2</sub>/O<sub>2</sub> fuel cells. These devices would be valuable power sources for airborne/spaceborne high power applications. The cells would be highly efficient at both partial and full load, be capable of very rapid start up and shut down, be lightweight and silent, and should have significant cold-start capability. The critical enabling technologies for this system are the development of high performance, long-lived chlorine gas diffusion electrodes and chloride-tolerant hydrogen anodes. Based on experimental work at PSIT, we believe that the achievement of these higher energy and power densities are feasible with this type of fuel cell configuration.

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