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A HIGH PERFORMANCE H₂-Cl₂ FUEL CELL FOR SPACE POWER APPLICATIONS

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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. PEMFC's 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 startup and shutdown. In addition, PEMFC's are lightweight and operate silently.

A significant impediment to the attainment of very high power and energy densities by PEMFC's is their current exclusive reliance on oxygen as the oxidant. Conventional PEMFC's 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 1.2V for the H₂-O₂ fuel cell is unattainable due to mixed potential effects at the oxygen electrode. Because of the high overpotential losses, cells using H₂ and O₂ are capable of achieving high current densities only at very low cell voltages, greatly curtailing their power output. Based on experimental 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 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 $1/2 H_2 + 1/2 Cl_2 \rightarrow HCl$. The standard cell potential for this reaction is 1.36V 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 non-polarizable 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 7M HCl at 25°C [2] from a mass transport corrected Tafel plot. We calculated an exchange current density of about 10^{-1} mA/cm². This value is approximately eight orders of magnitude greater than the exchange current density for oxygen reduction on platinum (10^{-9} mA/cm²).

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Relatively little research has been reported on hydrogen chlorine fuel cells. Recent research has focused on hydrogen/chlorine regenerative fuel cells for load leveling applications [3-7]. The regenerative fuel cell application, although related, is quite different from the H_2-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 H_2-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 decreases 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 DOE Phase II SBIR Program (Contract No. DE-AC02-86ER80366), PSIT developed a hydrogen/chlorine 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 1) the kinetics of chlorine reduction on several catalysts; 2) the actual polarization behavior of a chlorine gas diffusion electrode; 3) the conductivity of a commercially available membrane in the environment of interest to our system; and 4) 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, Cl_2 and chloride-tolerant H_2 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 H_2 oxidation.

We have measured current-potential curves for Cl_2 reduction at 23°C in 3M HCl on a number of different electrocatalysts in a gas diffusion electrode configuration. These electrocatalysts included: 1) high surface area (HSA) carbon black (Ketjen EC300J, Akzo Chemie); 2) heat treated HSA carbon black (Graphitized Ketjen); 3) low-loading (0.5 mgPt/cm^2) carbon-supported Pt; and 4) high surface area lead ruthenate mixed metal oxide. The polarization behavior of these materials is shown in Fig. 2. The best Cl_2 reduction performance was observed for the supported platinum electrocatalyst. These results indicate extremely low polarization behavior (70 mV at 1 A/cm^2) for the supported platinum electrode compared to that of O_2 , which does not even register a current under similar conditions. The measured rest potential of 1.29V shows a mixed potential loss of only 70 mV from the equilibrium value of 1.36V, 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 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_2 - Cl_2 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 Pt gas diffusion electrode structure with Nafion and coat the individual Pt 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 Pt surface area measurements on electrodes treated with Nafion for 30s and 12 hr. These are compared with results for untreated electrodes that were presoaked in a water/alcohol solution for 30s and 12 hr, respectively, to facilitate wetting upon immersion in the chloride test solutions.

No effect of chloride was seen with any electrode until the 0.1M chloride concentration. At this value, the standard anode presoaked for 12 hr suffered a 47% reduction in surface area, from 112 to $59 \text{ m}^2/\text{g}$. 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 0.1M on the untreated anode presoaked for 30s was probably lost due to incomplete wetting of the electrode.

At 1M chloride ion concentration, the surface area of both untreated anodes decreased, while the Nafion coated anodes exhibited little change. This behavior in 1M 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 to a loss of surface area for the uncoated anode of greater than 75%.

H_2 - Cl_2 PEMFC SYSTEM PERFORMANCE

To examine the relative merits of the H_2 - Cl_2 PEMFC system compared to the H_2 - O_2 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_2 - Cl_2 PEMFC will significantly outperform the H_2 - O_2 PEMFC. For mission lifetimes of 1 min, 1 hr, and 10 hr, we conservatively estimate the energy and power densities of the H_2 - Cl_2 PEMFC system to be, respectively, 20 Wh/kg and 1200 W/kg at 0.73V, 152 Wh/kg and 152 W/kg at 1.12V and 199 Wh/kg and 20 W/kg at 1.26V. These values are, respectively, 2, 1.5, and 1.33 times greater than the corresponding values optimistically estimated for an H_2 - O_2 PEMFC system based on state-of-the-art performance recently reported by Ballard Power Systems (BPS) [12]. For lifetimes greater than 10 hr, the energy and power densities of the H_2 - Cl_2 system asymptotically approach 1.3 times those of the H_2 - O_2 system. It is significant that, according to Appleby [13], the energy density figure of 152 Wh/kg (and greater) for the 1 hr mission (or longer) "exceeds the energy available from any known secondary battery, including sodium-sulfur." Also note that the energy density of the H_2 - Cl_2 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^2 (0.25 ft^2) each and weighs 45 kg as suggested by BPS [12]. The assumed mass significantly affects the estimates only for mission lifetimes less than 1 hr; for longer missions the mass of reactants and storage tanks predominates. The latter masses were taken from an Air Products catalog and are 0.112 kg/mol for Cl_2 , 0.190 kg/mol for O_2 , and 0.206 kg/mol for H_2 . 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 volts, and, P is the stack power in kilowatts.

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 0.985V and I_p is 1250A. 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 $V^0 = 1.34\text{V}$ (our measured room temperature value of 1.29V plus 50 mV Nernst gain for operating at 6 atm) and a projected value for I_p of 1943A based on 80 mV loss at 232A (we measured 70 mV at 1 A/cm²). 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 much more reversible than those of oxygen. The theoretical open circuit potential of a hydrogen-chlorine cell is about 160 mV higher than that of hydrogen-oxygen. 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 Cl_2 reduction on smooth Pt is about eight orders of magnitude greater than that of O_2 , and our measurements show much smaller overpotential losses at high current densities for Cl_2 than for O_2 . A $\text{H}_2\text{-Cl}_2$ 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 H_2 oxidation and Cl_2 reduction kinetics combined with the large freezing point depressions of concentrated HCl should give the $\text{H}_2\text{-Cl}_2$ PEMFC significant cold start capability.

CONCLUSIONS

The $\text{H}_2\text{-Cl}_2$ 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 $\text{H}_2\text{-Cl}_2$ PEM fuel cell could yield a system with power and energy densities inherently greater than currently available in $\text{H}_2\text{-O}_2$ 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 startup and shutdown, 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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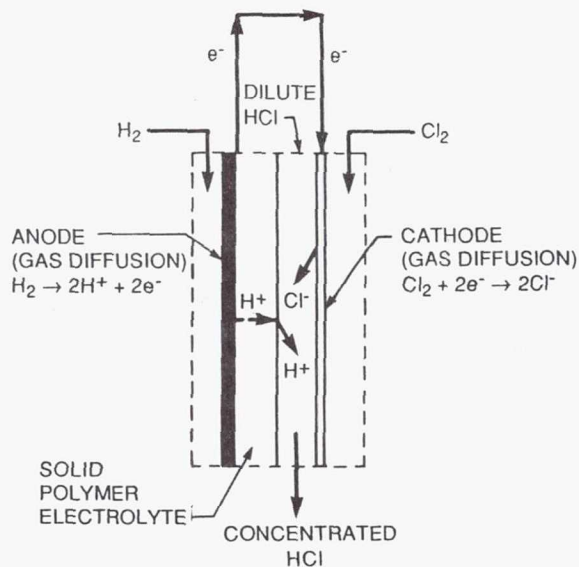


Fig. 1.—Schematic of H₂-Cl₂ Fuel Cell Using a Gas Diffusion Cl₂ Electrode with a Flowing Electrolyte. A captive electrolyte system for short-term applications is also an option.

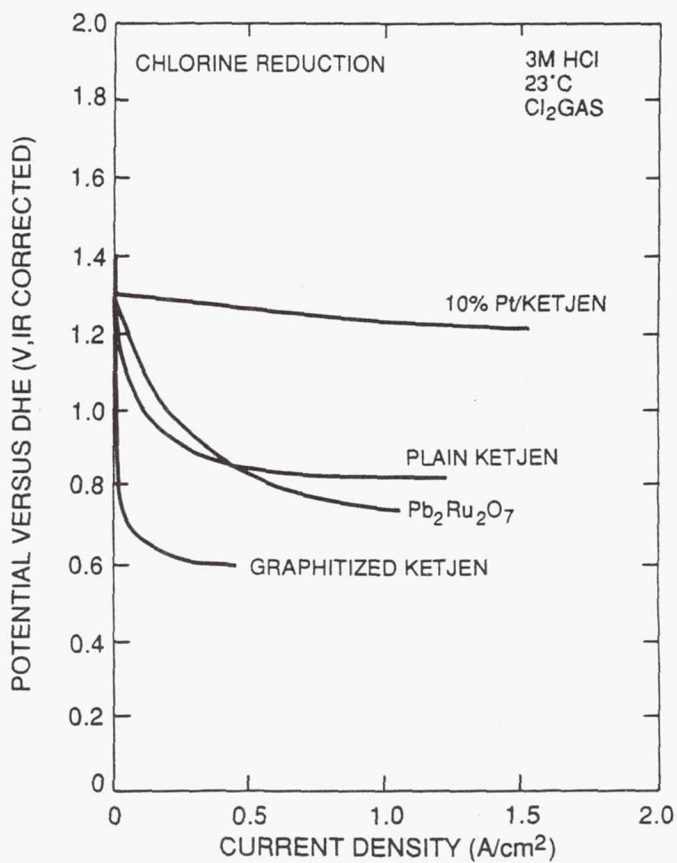


Fig. 2.—Chlorine Reduction Polarization Data in 3M HCl at 23°C with (a) 10% Pt/Ketjen, (b) Plain Ketjen, (c) Graphitized Ketjen and (d) lead-ruthenium oxide. Maximum current density here is determined by IR drop of the half-cell, not by electrode behavior.

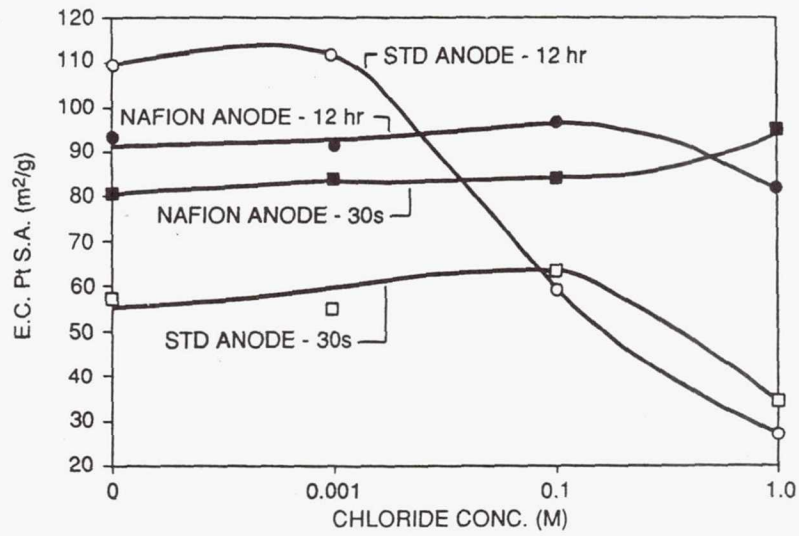


Fig. 3.—Results of Chloride Tolerance Study of Uncoated and Nafion Coated Standard Platinum Anodes

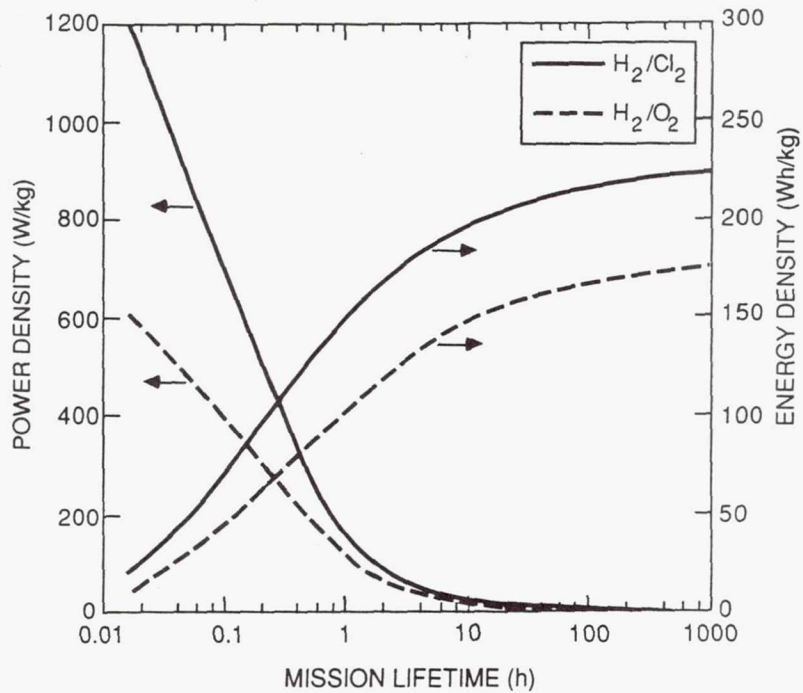


Fig. 4.—Estimated Optimum Power and Energy Densities Versus Mission Lifetime for PEMFC Systems

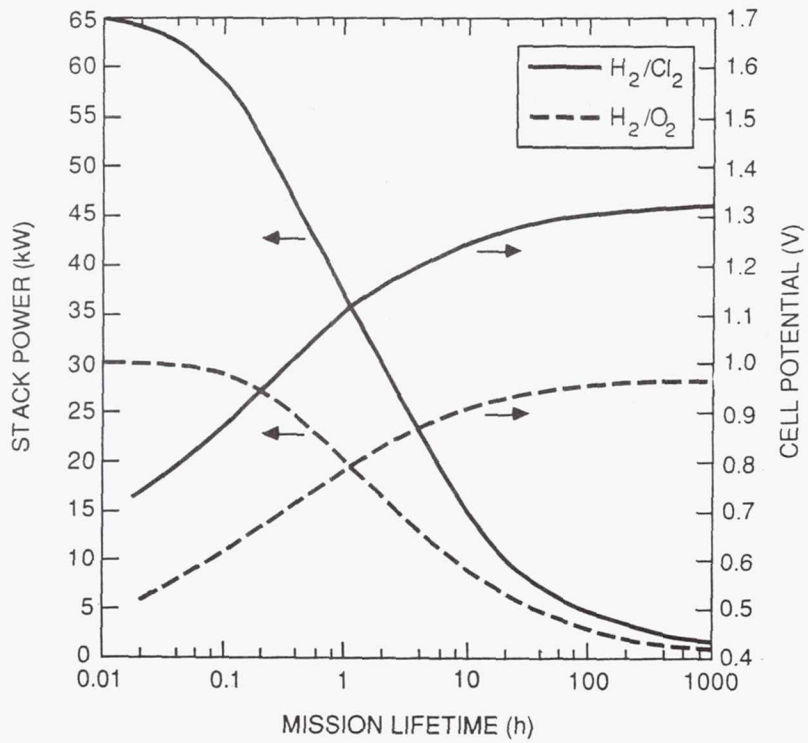


Fig. 5.—Estimated Optimum Cell Voltage and Stack Power Versus Mission Lifetimes for PEMFC System