

UCRL-JC-131087
PREPRINT

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This paper was prepared for submittal to the
Department of Energy Hydrogen Program Review
Arlington, VA
April 28-30, 1998

June 24, 1998



Lawrence
Livermore
National
Laboratory

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REGENERATIVE FUEL CELL SYSTEMS R&D

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Abstract

Regenerative fuel cell (RFC) systems produce power and electrolytically regenerate their reactants using stacks of electrochemical cells. Energy storage systems with extremely high specific energy (>400 Wh/kg) have been designed that use lightweight pressure vessels to contain the gases generated by reversible (unitized) regenerative fuel cells (URFCs). Progress is reported on the development, integration, and operation of rechargeable energy storage systems with such high specific energy. Lightweight pressure vessels that enable high specific energies have been designed with performance factors (burst pressure * internal volume / tank weight) >50 km (2.0 million inches), and a vessel with performance factor of 40 km (1.6 million inches) was fabricated. New generations of both advanced and industry-supplied hydrogen tankage are under development. A primary fuel cell test rig with a single cell (46 cm² active area) has been modified and operated reversibly as a URFC (for up to 2010 cycles on a single cell). This URFC uses bifunctional electrodes (oxidation and reduction electrodes reverse roles when switching from charge to discharge, as with a rechargeable battery) and cathode feed electrolysis (water is fed from the hydrogen side of the cell). Recent modifications also enable anode feed electrolysis (water is fed from the oxygen side of the cell). Hydrogen/halogen URFCs, capable of higher round-trip efficiency than hydrogen/oxygen URFCs, have been considered, and will be significantly heavier. Progress is reported on higher performance hydrogen/oxygen URFC operation with reduced catalyst loading.

Introduction

The LLNL effort to develop electrochemical energy storage systems occupies a crucial regime in the hydrogen technologies' adoption process, between pure research/conceptual feasibility and near-term demonstrations of commercial systems. This effort leaves as many component innovations as possible to others, and seeks to integrate the best systems from the highest performance, readily procurable components. The integration research and component testing being undertaken has already uncovered many operational and design issues that might hinder the adoption of breakthrough technologies being funded by the DOE and NASA. A focus on delivering energy storage to the most weight-sensitive applications (aircraft and spacecraft) ensures that key technologies will be properly implemented and combined to perform in real, upcoming vehicle tests.

The two key technologies that LLNL is aggressively implementing are proton exchange membrane (PEM)-based RFCs and high-performance tankage for storing compressed hydrogen and oxygen gases. Tankage built from available technologies must be lightweight and must cope with volume penalties, gas permeation, and moisture handling to adequately furnish the breakthrough levels of specific energy that RFC systems offer. Such multidisciplinary specifications have yet to be combined in the form of a commercial product. Were it not for LLNL's role as integrator leading industry, and as technical monitor promoting relevant specifications from within DOE-funded demonstration efforts in industry, such functional combinations of component performances would be years rather than months away. In particular, the DOE PRDA funded at Thiokol is on track to deliver vehicle-compatible hydrogen test tanks to support the Ford P2000 demonstration vehicle early next year. The supervision of and close interaction with this industrial demonstration project is one important example of the real effort DOE is sponsoring at LLNL to bridge research into demonstrations.

Another DOE-funded industrial demonstration effort, with Proton Energy Systems as prime contractor, has recently been funded to introduce PEM-based energy storage into electrical utility applications. Besides monitoring this field demonstration, LLNL will be directly supporting Proton Energy Systems's technology development by testing electrolyzer and URFC cell stacks. In the cases of Proton Energy Systems, Thiokol, and Hamilton Standard (which currently offers the most advanced electrochemical components) LLNL has achieved close cooperation with industrial partners who hold the intellectual property. With these partners, LLNL is jointly developing systems relevant to a wide spectrum of applications, as depicted in Figure 1. These systems include high altitude long endurance (HALE) solar rechargeable aircraft (SRA), zero emission vehicles (ZEVs), hybrid energy storage/propulsion systems for spacecraft, energy storage for remote (off-grid) power sources, and peak shaving for on-grid applications (Carter 1998, de Groot 1997, Mitlitsky 1998, Mitlitsky 1996-a, Mitlitsky 1996-b, Mitlitsky 1996-c, Mitlitsky 1996-d, Mitlitsky 1994, Mitlitsky 1993). Figure 2 illustrates the original application for this set of innovations: solar powered aircraft. This aircraft (Pathfinder) set the altitude record (71,500 ft) for all propeller-driven aircraft on July 7, 1997 (Mitlitsky 1998, NASA 1997).

Energy Storage Systems

Requirements for RFC energy storage systems are similar across a wide range of applications. Although stationary applications generally are not mass sensitive, they join a cluster of mobile, vehicular, and transportable applications that might advantageously store and retrieve energy with RFC systems. Those applications that are most mass sensitive are most likely to find RFC

systems an enabling technology. The LLNL RFC Systems effort is pursuing the most mass sensitive applications where their advantage will be clearest compared to secondary batteries. LLNL has also considered RFC systems that use hydrogen/air or hydrogen/halogen chemistries instead of hydrogen/oxygen. Both of these alternatives may emerge as advantageous in some stationary applications, as discussed in the **RFC Systems** section herein.

The energy storage requirements of a solar rechargeable aircraft (SRA) prompted LLNL to commission a study of secondary batteries (Arthur D. Little 1993). Although its predictions for lithium/ion and nickel metal hydride (NiMH_x) batteries have recently been adjusted upward, the basic result still holds in favor of RFC systems. Table 1 compares Specific Energy, a fundamental performance measure of any energy storage technique, and distinguishes between theoretical and packaged performance for various battery chemistries.

Table 1: Specific Energies for URFC and Rechargeable Batteries

| Battery System | Theoretical Specific Energy [Wh/kg] | Packaged Specific Energy [Wh/kg] | Comments |
|-------------------------------------|-------------------------------------|----------------------------------|-------------------------------------------|
| H ₂ /O ₂ URFC | 3660 | 400-1000 | URFC with lightweight pressure vessels |
| Li-SPE/MO _x | 735 | 220 | Novel packaging for unmanned system |
| Ag/Zn | 450 | 200 | Excess Zn required, low charge rate |
| Li/LiCoO ₂ | 735 | 150 | Poor cycle life, high capacity fade |
| Li/AlFeS ₂ | 515 | 150 | ≥400°C thermal management |
| Na/S | 1180 | 150 | ~350°C thermal management |
| Li/TiS ₂ | 470 | 130 | ~50% DOD for high cycle life (900 cycles) |
| Li/ion | 700 | 100 (135)^a | Projection revised November 1996 |
| Ni/Zn | 305 | 90 | Excess Zn required, low specific energy |
| Ni/MH _x | 470 | 70 (85)^a | Projection revised November 1996 |
| Ni/H ₂ | 470 | 60 | Low specific energy |
| Ni/Cd | 240 | 60 | Low specific energy |
| Pb/acid | 170 | 50 | Low specific energy |

Survey by A.D. Little, Inc., July 1993 for LLNL, excluding URFCs

^a Projections revised in November 1996 (private communications, Brian Barnett)

Figure 3 sketches the distinction between total reactant mass that could theoretically store a chemistry-limited specific energy, and packaged performance of a battery technology. Due to reaction kinetics, not all reactants are accessible, so that batteries introduce depth of discharge limitations which fuel cells can ignore. Because fuel cell systems store their reactants outside the electrochemically active cell stack, their specific energy is limited by the mass of the reactant

containers. Such containers do not need to satisfy the complex requirements of battery packaging, but they must be sufficiently chemically inert and impermeable

LLNL is developing containers suitable for storing gaseous hydrogen and oxygen in the most mass sensitive applications. These containers are pressure vessels derived from aerospace pressure vessel technology. The earliest example of actual, hydrogen impermeable tankage suitable for vehicular energy storage applications is likely to be produced by Thiokol later this year, acting in close collaboration with LLNL under a DOE PRDA. Figure 4 illustrates Thiokol's conformable two cell tank configuration now being adapted from compressed natural gas (CNG) to hydrogen service. Figure 5 illustrates a more advanced configuration of conformable tank, employing three cell tanks that provides the best fit for Ford's P2000 demonstration vehicle.

Much of the complexity of battery technology is dispensed with in RFC systems, where a Proton Exchange Membrane (PEM) cell stack can convert energy between electrical and chemical forms without having to store energetic chemicals as part of the electrode package. LLNL has chosen to explore the Unitized Regenerative Fuel Cell (URFC), since detailed mass projections showed energy storage system mass will be significantly reduced by using the same cell stack to convert energy in both directions. Slight efficiency compromises could accompany the choice of a particular set of catalysts (on oxygen and hydrogen sides of a PEM cell membrane) that must serve both electrolysis and fuel cell operating modes. To date, no such performance compromises have been observed, while characterization of unidirectional cell stacks, especially pure electrolyzers, is soon to begin at LLNL in parallel with URFC testing. The sequence of electrochemical progress at LLNL, including recent groundbreaking results, will be presented after progress is reported in the various other components and operation of RFC Systems.

Tankage

Tankage mass puts a ceiling on RFC energy storage density. Even if the cell stack and ancillaries weigh nothing, system specific energy will be diluted by the mass required to contain reactants. Because cryogenic storage, especially of hydrogen, is such a challenging frontier in itself, a different DOE funded effort is underway at LLNL to explore its expected characteristics (Aceves 1998). The significant amount of thermal energy that must be transferred to employ cryogenic hydrogen suggests that cryogenic energy storage media will first find application in primary power plants. Thus this system integration effort is pursuing the most mass effective storage of gaseous hydrogen and oxygen.

The need for advanced development of compressed hydrogen tankage technology becomes apparent when the specifications commensurate with energy storage applications are combined. Aerospace tankage technology can take advantage of the best composite materials to contain the gas pressure, but relies on liners for permeation control that are massive, ill-conceived, and pose additional mass penalties for cycle life. Other forms of tankage simply do not compete strongly with the best composites, as shown in Figure 6. That figure compares a performance factor that is proportional to contained gas mass over tank mass independent of tank scale. (In ideal gases the performance factor sizes tank mass independent of operating pressure as well.) Detailed point designs showed the advantages of developing a tank liner technology that could contain the

most reactant (esp. hydrogen) for a given tank mass, and the advantages of a thin liner technology appear in the rightmost bar of Figure 6

Figure 7 shows LLNL's previous development of thin liner technology under the DOE/Ford program. These vessels use lightweight bladder liners that act as inflatable mandrels for composite overwrap and provide the permeation barrier for gas storage (Mitlitsky 1998, Mitlitsky 1996-a, Mitlitsky 1996-c, Souers 1986). Bladders are fabricated using materials which are compatible with humidified, electrolyzed gases, and are designed to be compatible with elevated temperatures that occur during fast fills or epoxy curing cycles. The cylindrical tank geometry is important not just for aircraft energy storage, wherein LLNL has been funded by NASA to develop runway-replaceable tank liners, but also to evaluate the potential of structural tankage. Effective specific energies for storage systems that also perform structural functions can be boosted several-fold above the predicted URFC system performance in Table 1.

Several thermal issues must be considered to design pressure vessels capable of fast filling with hydrogen. Gas compression during pressure vessel filling results in gas heating which can result in underfilling and/or overpressurization. The temperature rise associated with filling a pressure vessel is related to the pressure ratio, fill rate, properties of the gas, thermal mass of the vessel and plumbing, and heat transfer coefficients. Large pressure ratios, rapid fill rates, hydrogen gas, and lightweight pressure vessels with poor heat transfer coefficient can result in large temperature rises. Neglecting heat transfer and the thermal mass of the vessel and plumbing, a study (Daney 1995) shows that for an infinite pressure ratio of an ideal gas, the temperature ratio for a fast fill is equal to the ratio of specific heats (which is 1.41 for hydrogen). By this criterion, a vessel with 300 K (27 °C = 81 °F) initial gas temperature would achieve a final gas temperature of up to 420 K (147 °C = 297 °F). Such worst case temperature rise would result in filling the tank to only 71.4% of rated capacity at the maximum operating pressure. The final gas temperature peaks can be worsened by high ambient temperature or gas lines that are already warm.

Temperature rise (underfilling) for natural gas vessels is less than for hydrogen due to lower ratio of specific heats (~1.32). Even so, by the criterion above a fast fill from 300 K would yield a temperature of 396 K (253 °F). A typical temperature rise to ~140 °F (333 K), from an initial temperature of 70 °F, for fast fills of compressed natural gas (CNG) into a vessel with an adiabatic inner wall has been reported (Kountz 1994). One of the main reasons for the discrepancy is due to the heat capacity of the pressure vessel (Mitlitsky 1998).

In order to package gaseous hydrogen into an automobile without enormous changes in vehicle layout, a different approach to tankage makes sense for volume-constrained systems. The LLNL effort is employing DOE funds in a high leverage opportunity to innovate this regime. The tankage technology closest to delivering hydrogen pressure vessels suitable for many mobile applications, including hydrogen-powered passenger vehicles, should soon exist through a development program underway at Thiokol. Thiokol is the most capable of the aerospace tankage suppliers, and has won the DOE PRDA to develop commercial hydrogen pressure vessel technology. LLNL serves as technical monitor in this development effort, and has intervened repeatedly to insure that Thiokol's developments are most likely to satisfy the true requirements of a hydrogen economy.

The hydrogen gas storage technology Thiokol is developing is most relevant to passenger vehicles, and is unlikely to do better than other aerospace tankage approaches at the most mass sensitive applications LLNL is pursuing. Thiokol anticipates its extraordinary expertise will allow it to withstand cheaper competitors because their development will produce non-axisymmetric pressure vessels it calls Conformable Tanks. Enroute to these unprecedented geometries, Thiokol has expended internal funds developing subscale prototypes that are conventional domed cylinders. LLNL tankage developments which should substantially improve the mass performance of high pressure hydrogen tanks can take advantage of the tooling and winding already developed at Thiokol. This existing capability enables LLNL to effectively pursue a new generation of thin tank liners, this iteration using rotational molding to avoid the problematic transition between a thin sidewall and a thick end dome.

Figure 8 provides a high-level roadmap of the advanced tankage developments underway at LLNL. Figure 9 shows earlier work on structural performance of cylindrical tanks suitable for thin bladder liners. Development of radical tankage is proceeding along this branch, and three others shown in Figure 8. Two other approaches with potentially higher payoff are receiving preliminary attention, besides the removable, cylindrical bladders and the rotationally molded liners. Linerless approaches offer potentially maximal weight savings, at the expense of a total change from the epoxy matrix formulations familiar to composite fabricators. Blow molding is a likely follow on process that can produce much thinner liners at minimal expense, however production volumes must grow several orders of magnitude to justify costly tooling and materials development. These later options are being pursued at a low level. Both main lines of advances in tankage, as well as an LLNL capability to test commercial hydrogen tanks, call for the creation of a new experimental facility at LLNL. Figure 10 is a picture of the explosion-proof room in that facility required to safely test unproven approaches to hydrogen tankage.

Thiokol Collaboration

Tankage development can only proceed so far before strenuous testing is required to prove new concepts. Figure 11 graphically illustrates the rigors of getting actual tanks to live up to predicted performance. The photogenic wreckage documents the first successful test, where burst pressures fell within 5% of Thiokol's prediction. Using Thiokol IR&D funds to reduce risks on the DOE PRDA, this subscale test program went through several rounds of alarming failures before this success, the previous failure mode damaged the test apparatus by spitting out its inadequately anchored boss. Technical risks continue to be run as various fiber and winding process variables remain to be reduced to predictability by the procedure illustrated in Figure 12.

LLNL has been steadily contributing expertise to the ongoing design and debugging of Thiokol's tankage developments under the DOE PRDA, while Thiokol has operated essentially without feedback in the part of their design that relies on their unique expertise. Figure 13 shows the completed fruit of Thiokol's non-axisymmetric design capability. This liner contour is compatible with an optimized design for the shape of composite wrapped layers that form a conformable tank's complicated end dome. Figure 14 shows Thiokol's finite element analysis that projects stresses in their end dome design, and outlines their approach to verifying the design code's prediction.

Much of the close collaboration between LLNL and the DOE tankage PRDA contractors, including Aero Tec Laboratories (ATL) and Thiokol, anticipates the difficult qualification of a liner suitable for resisting hydrogen permeability, matching the process requirements of subsequent composite overwrap, and capable of a high-cycle-life interface with the tanks boss/end detail. Although Thiokol is contributing most of the design, and considerable intellectual property, to the boss, all three organizations have learned the necessity of close communication on liner design. The difficulties of liner material selection were initially underestimated by all the available experts. A screening process is currently underway which should select a liner material suitable to proceed into rotational molding. This screening process relies on a testing contractor, Southern Research Institute (SRI), that has a long history for furnishing test results to Thiokol's specifications. Figure 15 summarizes Thiokol's approach to down-selecting the liner material based on SRI's hydrogen permeation measurements.

The LLNL effort to develop the next generation of advanced hydrogen tankage was able to take advantage of existing SRI capability and further a broader understanding of hydrogen permeability. Although Thiokol is internally funding a new facility at SRI capable of permeation testing at high pressure with hydrogen, SRI offered to employ its 200 psi permeation test capability under direct contract to LLNL during the short interval before the Thiokol work commenced. LLNL took advantage of this interval to procure ASTM-traceable calibration for all subsequent measurements, to confirm previous measurements made at LLNL on LLNL-developed liners, and to further study hydrogen permeation through thin films. Figure 16 shows the 200 psi permeation test rig at SRI that performed LLNL's measurements.

The graph in Figure 17 not only confirms the hydrogen permeability (of P-03 liner material developed at LLNL) using a different technique, it extends the earlier LLNL results to a range of pressures, temperatures, and specimens. Although the high pressure rig at SRI will be required to confirm a material's acceptability as a thick liner for high pressure tankage, further LLNL experiments on the low pressure rig at SRI will support the development of advanced liners.

RFC Systems

Although tank masses dominate the specific energy performance of RFC systems, many other components and operations must be integrated to deliver functional energy storage systems. This integration research has been a continual learning process, with the past year's progress built on a foundation of developments already proven and listed in Figure 18. Figure 19 brings this list of accomplishments up to date.

URFCs should be capable of higher specific energy and less complexity (due to reduced parts count) compared with RFCs using separate (dedicated) fuel cell and electrolyzer stacks. However, there is an erroneous presumption that URFCs are not capable of high cycle life, due to the lack of well publicized data showing tests lasting more than ~25 cycles. Results from tests reported recently (Mitlitsky 1998) are an existence proof that URFC cells can be cycled repeatedly (>2000 cycles) without significant degradation (less than a few percent). These tests are also an existence proof that bifunctional catalysts can operate reversibly without significant degradation.

Even though bifunctional catalysts will not be simultaneously optimized for both oxidation and reduction reactions, URFC systems will not necessarily be less efficient than RFC systems using dedicated stacks. Although it is true that bifunctional catalysts may have slightly reduced performance in either the oxidation or reduction reaction (depending on catalyst composition, which may be optimized for a given system application), this will result in a modest round-trip efficiency decrease per unit of active area for the URFC stack, and not necessarily an efficiency decrease for the entire URFC system. It should be realized that the efficiency of a dedicated fuel cell (FC) during the charge cycle is zero, and likewise, the efficiency of a dedicated electrolyzer (EC) during the discharge cycle is also zero. Therefore, it is more reasonable to compare the efficiency of RFC systems which use similar active areas. By this criterion, the active area for the URFC stack is equivalent to the sum of the active areas for the dedicated FC and EC stacks combined. In such a comparison, a given power setting (either input or output) will result in less power per unit active area for the URFC by virtue of the larger active area utilized in each mode of operation. The operational current densities in the URFC will be below the corresponding current densities in the dedicated FC/EC stacks, resulting in an improved voltage efficiency for the URFC system. This efficiency improvement may even overwhelm the efficiency reduction caused by using compromise catalysts (Mitlitsky 1998).

URFCs may have other system advantages over dedicated FC/EC stacks in cases where ambient temperatures are prone to be below freezing conditions and where the typical system operation cycle requires near-continuous operation of either charge or discharge without long periods of system idling. In such cases, URFC stacks will stay warm by virtue of their continuous operation, whereas dedicated FC/EC stacks will require additional insulation and/or parasitic power to maintain the non-operating stack at required temperatures.

The electrochemical reactions for FC and EC operations for hydrogen/oxygen based systems are depicted in Figure 20. The URFC can be designed for electrolysis with water fed from either the anode (oxygen side) or the cathode (hydrogen side). For cathode feed electrolysis, a single phase separator is used in the hydrogen/water recirculation loop. Water must then diffuse through the cell to the oxygen side in order to be split. This necessary flow is decreased by an opposing flow of water caused by proton pumping, whereby each proton migrating through the membrane toward the cathode must be accompanied by at least four water molecules (Appleby 1986). This creates a situation where cell drying at the anode may result, especially at high current densities. Anode feed electrolysis provides excess water at the anode, avoiding the drying (at high current densities) that may be caused by proton pumping. For anode feed, phase separators are required in both the anode/water and the cathode/water recirculation loops, which add complexity and weight to the system (Mitlitsky 1998).

Other URFC chemistries are possible, such as hydrogen/halogen (Beaufriere 1977, McElroy 1979, McElroy 1977). These are of interest because they are capable of higher round-trip electrical efficiencies. Since they may be more than an order of magnitude heavier for comparable energy content, they are not of interest for mobile applications, but are considered for stationary applications. Since halogens and their acids are corrosive and toxic, safety considerations may limit the use of hydrogen/halogen URFCs to specific niches where the improved efficiency is an overriding consideration. Efficiency of hydrogen/halogen URFC systems is a function of acid concentration and current density (McElroy 1979). Unlike for water cycle URFCs,

hydrogen/halogen stacks can be nearly 100% efficient, if operation is restricted to very low current densities, where FC and EC polarization curves approach one another. Greater than 90% electric-to-electric (ETE) voltage efficiency was achieved at low current density (108 mA/cm^2) in the 1970s (McElroy 1979). It was estimated that system-level parasitics would reduce the actual round-trip energy storage efficiency by $\sim 10\%$ due to pumping power, current inefficiencies, and power conditioning inefficiencies (Mitlitsky 1998).

Electric utilities are interested in peak shaving energy storage systems to maximize utilization of existing base load electric generators and to postpone the installation of new generating equipment. Lead acid batteries are a preferred utility energy storage technology. Unlike the lead acid battery, RFCs uncouple power and energy ratings. This allows the RFC to accommodate weekly and even seasonal cycles. The H_2 /bromine URFC has been demonstrated in single cells for up to 4000 hours with 80% round-trip energy storage efficiency, and showed stable cyclic performance in the early 1980's for a Boeing MX missile program (Nutall 1982). Scale up of cells to $>0.23 \text{ m}^2$ (2.5 ft^2) and minimization of corrosion currents have yet to be demonstrated.

Less conventional stationary applications currently use lead acid batteries to store electric energy for remote off-grid applications. Primary electricity for these applications can come from solar, wind, or diesel generators. Up to ~ 3 days of energy capacity are typically stored in the lead acid systems. H_2/O_2 or H_2 /air URFC systems will have longer life, could have lower life cycle cost, as well as allowing weekly and seasonal energy storage capabilities. The selection of H_2/O_2 versus H_2 /air URFCs depends on a number of considerations. URFC systems based on H_2/O_2 have higher performance per unit area of membrane, do not need oxidant compressors, can operate completely closed cycle with little maintenance, are capable of slightly higher efficiency, but require $\sim 50\%$ more tankage to store oxygen. H_2/O_2 systems are generally preferred in cases where the compressed oxygen storage does not pose a significant safety hazard (Mitlitsky 1998).

Daytime shortages of electrical power (brown-outs or black-outs) are becoming more frequent in industrial countries. Total energy supplies are adequate on average, but daytime peaks cannot be sustained. A small H_2 /air URFC could provide the utility customer with energy during peak power periods. With sufficient numbers of individual home owner units in place, this significant pressure on electric utilities would be reduced. Hydrogen/halogen URFC systems with an attractive mix of high efficiency and low capital cost for utility load leveling are being investigated enroute to a demonstration facility.

URFC systems with lightweight pressure vessels have been designed for automobiles and are expected to be cost competitive with primary FC powered vehicles that operate on hydrogen/air with capacitors or batteries for power peaking and regenerative braking (Mitlitsky 1994). URFC powered vehicles can be safely and rapidly (< 5 minutes) refueled from high pressure hydrogen sources, when available, to achieve driving ranges in excess of 360 miles (600 km). The employment of URFCs would save the consumer the entire capital cost of a home hydrogen generation unit. That consumer would now be able to electrically recharge at any available electrical source, instead of being tethered to a single home electrolysis unit. URFC-powered automobiles would still be able to rapidly refuel by direct hydrogen transfer when a hydrogen infrastructure becomes available.

Ancillaries

The URFC test facility at LLNL has been described elsewhere (Mitlitsky 1998). A primary fuel cell test rig from Hamilton Standard with a single cell (46 cm² active area) was modified for use as a URFC test rig. Hydrogen and oxygen are supplied by source bottles, or by recycle bottles that can be filled by electrolysis. This rig has undergone nearly continuous upgrading. In the core of that rig is a single cell 'stack' which Hamilton Standard used for internal development in the early 1980s. Figure 21 is a photograph of the central cabinet within this rig. Nearly triple the original fluidic component count has been added to this rig to allow testing of URFCs. Figure 22 is a fluid schematic indicating the current flow capabilities and features of this rig. The wealth of unusual components indicates how many operating characteristics and design issues have already been encountered. The last ~25% in fluidic component count was added to the rig, producing the symmetric section with identical hydrogen and oxygen phase separators, to enable testing of anode feed electrolysis.

The current LLNL test rig has been upgraded to a space and modification limit. Not only is expansion space missing within its equipment case and hood, the density of its current components poses major risks to its test capability if the improvements necessary to test higher power levels are attempted. Therefore the existing rig's test capability will be left intact to study the electrochemical components discussed below, and a second generation of rig hardware has commenced construction. This new generation is intended to operate in the new facility, under much larger hoods with the capacity to test multi-kilowatt components. Figure 23 shows the first use of next-generation valves, which are being tested in two critical locations on the existing test rig. It was desirable to introduce these valves as the final modification to the existing rig's plumbing because their high pressure ratings (for blocking flow) in both directions have proved to be important in these two locations, minimizing the amount of water that is released into gas plumbing as a result of shifting into electrolysis modes. Considerable progress in LLNL capabilities and understanding accompanied these rig upgrades, as well as a protracted period of debugging that suggested many ways to improve a second generation rig.

The list in Figure 19 summarizes the accomplishments that have already occurred in FY98. This list collects the many facets of progress being made at LLNL toward deploying and understanding RFC energy storage systems. It includes the development of appropriate tankage, the ability to properly specify PEM stacks, and the development of many unique ancillary components. Except for the ongoing electrochemical investigations being performed with the existing rig, the next stage in many of these facets awaits a new facility. Figure 24 shows the new facility at LLNL prior to occupancy. The radiation-hardened room with two steel doors is ideal for the explosion-proof tank testing mentioned above. The entire facility has yet to be connected to a ductwork, blower, and stack system of sufficient capacity to safely exhaust the worst-case hydrogen release, but it is anticipated on-line and safety-approved later this year.

URFC Experiments and Results

Experiments with the LLNL URFC test rig were limited within a parameter space of "safe" testing that could be performed while unattended. The maximum allowable working pressure

(MAWP) of the hydrogen side of the system is 80 psig (0.653 MPa), and the MAWP for the oxygen side is 160 psig (1.20 MPa). For safety reasons, the oxygen pressure was required to be slightly higher (consistently) than the hydrogen pressure. Maximum operating temperature of $\sim 90^\circ\text{C}$ is limited by some of the solenoid valves in the system. The H_2 and O_2 gas flows in the test rig are plumbed for flow through (rather than dead-ended) FC operation. High flow rates can cause some gas to flow past the membrane and electrode assembly (M&E) without reacting. Flow and pressure settings in the test rig were initially somewhat variable due to lack of feedback control. Data logging accuracy can be improved by measuring under conditions of high gas flow, in order to make measurements insensitive to slight flow variations.

When switching from electrolyzer to fuel cell mode, short drying cycles may be required to remove the small amount of water that has been trapped in the "dead space" of the cell after water supply has been turned off. For cells requiring very rapid switching times, this dead space should be minimized to reduce drying time. For the cell configuration being tested (which was designed initially for dedicated fuel cell operation and converted to a URFC without considering this design parameter), it was determined that 2.0-2.5 minutes at 240 ASF (250 mA/cm^2) were required for drying. Drying time can be reduced under the current configuration by increasing current density. By increasing the drying current density to $>1000\text{ ASF}$ ($>1.08\text{ A/cm}^2$), drying time was reduced to 25-30 seconds. Using this rapid drying technique, round-trip cycle times of <1 minute were demonstrated on URFCs at current densities in excess of 1000 ASF (1.08 A/cm^2) in both fuel cell and cathode feed electrolysis modes. The drying procedure has also been accomplished in ~ 15 seconds using a current density of 1.5 A/cm^2 . It is expected that redesign of the cell, catalyst, and drying procedure could reduce this drying time to a fraction of a second.

The method of cycle testing URFC cells at LLNL was described recently (Mitlitsky 1998). Cycle testing of a single cell URFC was started in November 1996 at LLNL. The test results for a single cell cycled 2010 times are presented in Figure 25 at four different current densities for both fuel cell (FC) and electrolyzer (EC) modes (eight curves total). This experiment accurately measured the cell voltage under repeatable conditions to determine the extent of cell degradation. Zero degradation would be reflected in horizontal curves (no change in voltage as a function of cycle life). If there was significant degradation due to cycling, the FC curves would display larger negative slopes and the EC curves would display larger positive slopes. The curves in Figure 25 show negligible degradation in both FC and EC performance, over a range of current densities; and are a higher fidelity and greater range of data compared to the earlier work at General Electric (Chludzinski 1973).

Another URFC membrane and electrode assembly (M&E) was installed and tested (cell #9734A). This cell had an internal resistance of $6.3\text{ milliohm}/46\text{ cm}^2$ active area at 297 K , a value much closer to the expected value for a good cell. Internal resistance was measured to be 3.8 milliohm at 188°F inlet temperature (360 K). A polarization curve for this cell is shown in Figure 26 at conditions which are very close to the highest temperatures and pressures allowable for the test rig in its present configuration. This figure proves that URFC cells can be cycled at $>1000\text{ ASF}$ ($>1.08\text{ A/cm}^2$) in both fuel cell and cathode feed electrolyzer modes using Nafion 117 membrane. This figure shows that cathode feed electrolysis may take place at relatively high current densities, despite the concern that cathode feed designs may be prone to membrane dry-out. Figure 26 also shows polarization curves for cell #LLNL01 that were cycle tested as

described above, in order to emphasize the performance improvement achieved in the cell design of cell #9734A (Mitlitsky 1998).

These results are an important milestone and a significant improvement over what has previously been demonstrated. Both of the cells (#9734A and #LLNL01) tested used Nafion 117 membrane and Hamilton Standard's E-5 catalyst, which is a proprietary mixture of platinum, platinum group metals, and their oxides. Catalyst loading was 4 mg/cm² per electrode in both cells. The reduced internal resistance of cell #9734A and its corresponding performance improvement is attributed to the use of a new porous plate.

LLNL recently started testing URFC cells using Nafion 105 membrane and reduced catalyst loading. Cell #9804A uses Nafion 105, Hamilton Standard's E-5 catalyst, and catalyst loading of 1 mg/cm² per electrode. Figure 27 shows the high performance polarization curve data taken on this cell at the same conditions that cell #9734A was measured under in Figure 26. Data from cell #9734A is replotted on the same curve as Cell #9804A in Figure 27 to highlight the performance improvement of cell #9804A. This figure shows that fuel cell operation on URFCs is feasible at current densities >2000 ASF (2.15 A/cm²). Cathode feed electrolysis data was limited to 1200 ASF due to cell dryout. Anode feed electrolysis data was taken at current densities >2000 ASF (2.15 A/cm²), but has not yet been approved for publication.

Figure 27 shows that reduced catalyst loading operation of PEM electrolyzers and URFCs is feasible, and shows that consumer markets that may require reduced catalyst loading to achieve inexpensive unit costs at high volume may be filled by PEM electrolyzers and URFCs. Experiments are continuing to reduce catalyst loading even further.

Acknowledgments

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract W-7405-Eng-48. This work was funded in part by Ballistic Missile Defense Organization, Ford Motor Company, LLNL Laboratory Discretionary Research Funds, NASA, and U.S. Department of Energy. This work was performed in conjunction with various organizations, including Aero Tec Laboratories (Ramsey, NJ), AeroVironment (Monrovia, CA), Brigham Young University (Provo, UT), Composite Solutions (Salt Lake City, UT), Directed Technologies Inc. (Arlington, VA), EDO Fiber Science Division (Salt Lake City, UT), Proton Energy Systems (Rocky Hill, CT), Thiokol Corporation (Brigham City, UT), and United Technologies, Hamilton Standard Division (Windsor Locks, CT). Figure 28 combines the logos of several of LLNL's industrial partners.

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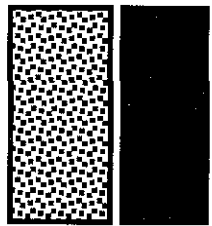
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Figure Titles

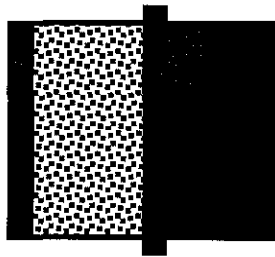
- Figure 1: URFCs with Lightweight Structure/Tankage Applications
- Figure 2: Solar Powered Aircraft Sets New Record (71,500 ft on 7/7/97)
- Figure 3: Theoretical and Packaged Specific Energies
- Figure 4: Thiokol's Conformable Tankage - Two Cell Prototype
- Figure 5: Thiokol's Three Cell Configuration for Ford P2000
- Figure 6: Performance Factor ($P_b V/W$) for High Cycle Life Cylinders
- Figure 7: High Performance Factor Bladder-Lined Tanks Fabricated
- Figure 8: Roadmap for LLNL Tankage Development
- Figure 9: Hybrid Structural Tanks Load Tested to Failure in Bending
- Figure 10: Explosion-Mitigation Room in New Facility
- Figure 11: Thiokol IR&D-Funded Subscale Testing
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- Figure 13: Finite Element Solid Model of Conformable Liner
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- Figure 16: Southern Research Institute (SRI) Permeability Test Rig
- Figure 17: SRI Confirms & Extends H_2 Permeance of LLNL's Laminate
- Figure 18: Past Results of RFC Project at LLNL
- Figure 19: Current Year Accomplishments / Status
- Figure 20: URFC Electrochemical Operating Modes
- Figure 21: URFC Test Rig at LLNL Demonstrated >2000 Cycles
- Figure 22: Current LLNL Test Rig Schematic
- Figure 23: Progress In PEM Ancillary Components Extends Functionality
- Figure 24: New Facility for URFC and Tankage Development
- Figure 25: URFC Cycle Test Demonstrated Negligible Degradation
- Figure 26: URFC Performance Improvement Reported in Energy & Fuels
- Figure 27: Higher Performance URFC Using Reduced Catalyst Loading
- Figure 28: Logos of LLNL's Industrial Partners

Theoretical



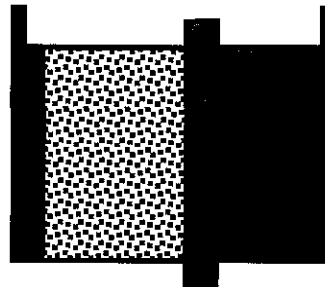
Stoichiometric
Reactants Only

Optimum



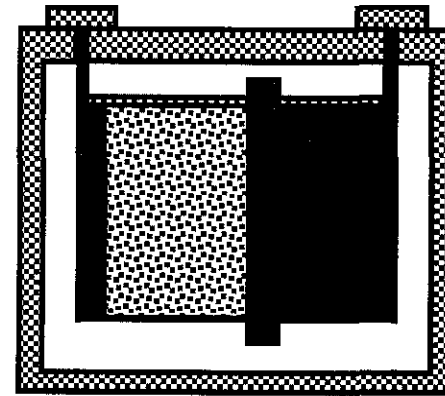
Stoichiometric Complete Cell
with Electrolyte, Separator,
and Current Collectors

Functional



Non-Stoichiometric for
Cycling Requirements

Packaged



Packaged for System

- Theoretical specific energy uses the weight of stoichiometric reactants only
- Stoichiometric complete cell adds weight of electrolyte, separator, and current collector required to draw current from the cell
- Functional cell adds weight of non-stoichiometric reactants to achieve required cycle life
- Packaged cell adds weight of packaging required for safe containment, shipping, handling, and extended life

Figure 3



THIOKOL
AEROSPACE & INDUSTRIAL TECHNOLOGIES

Figure 4

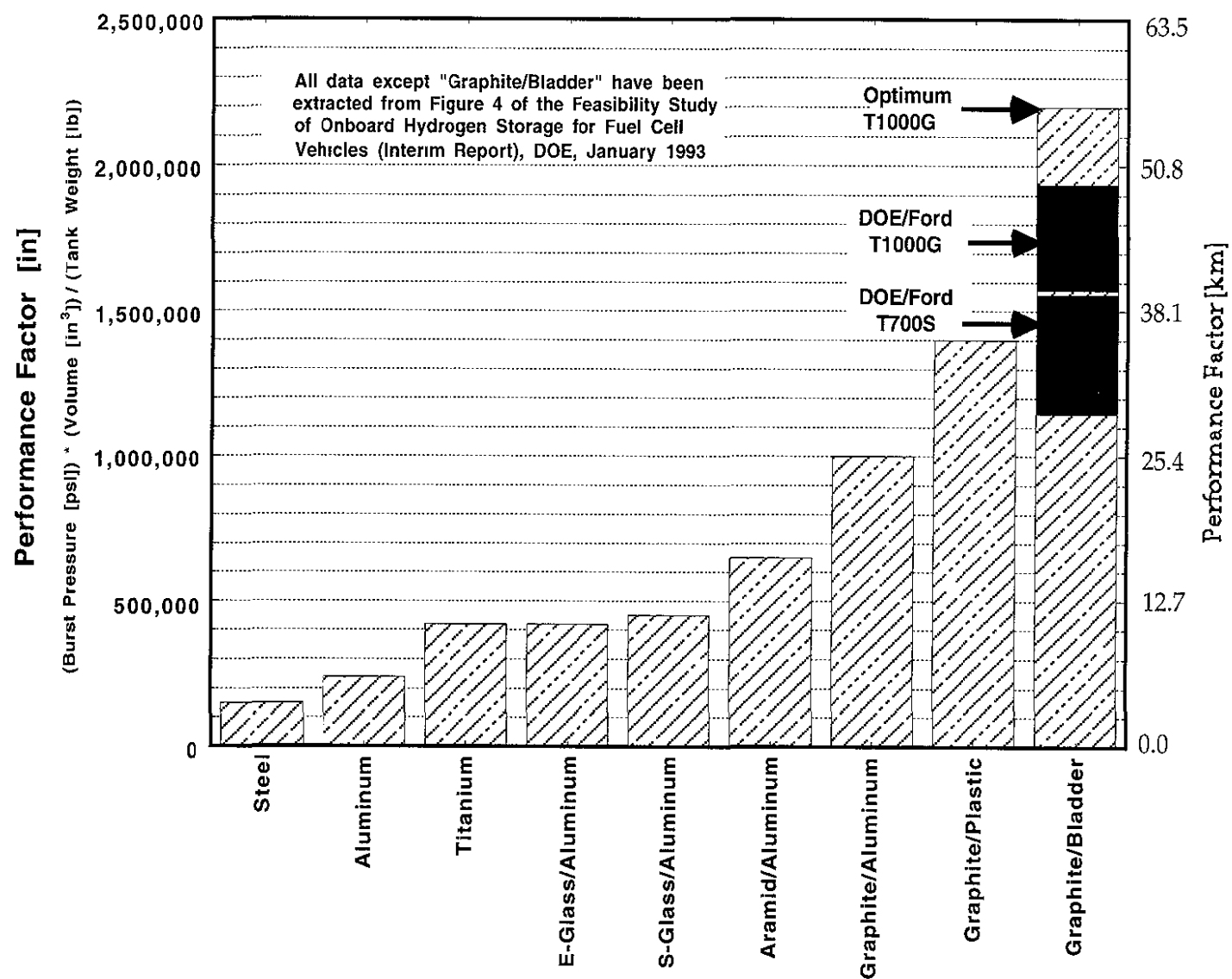


Figure 6

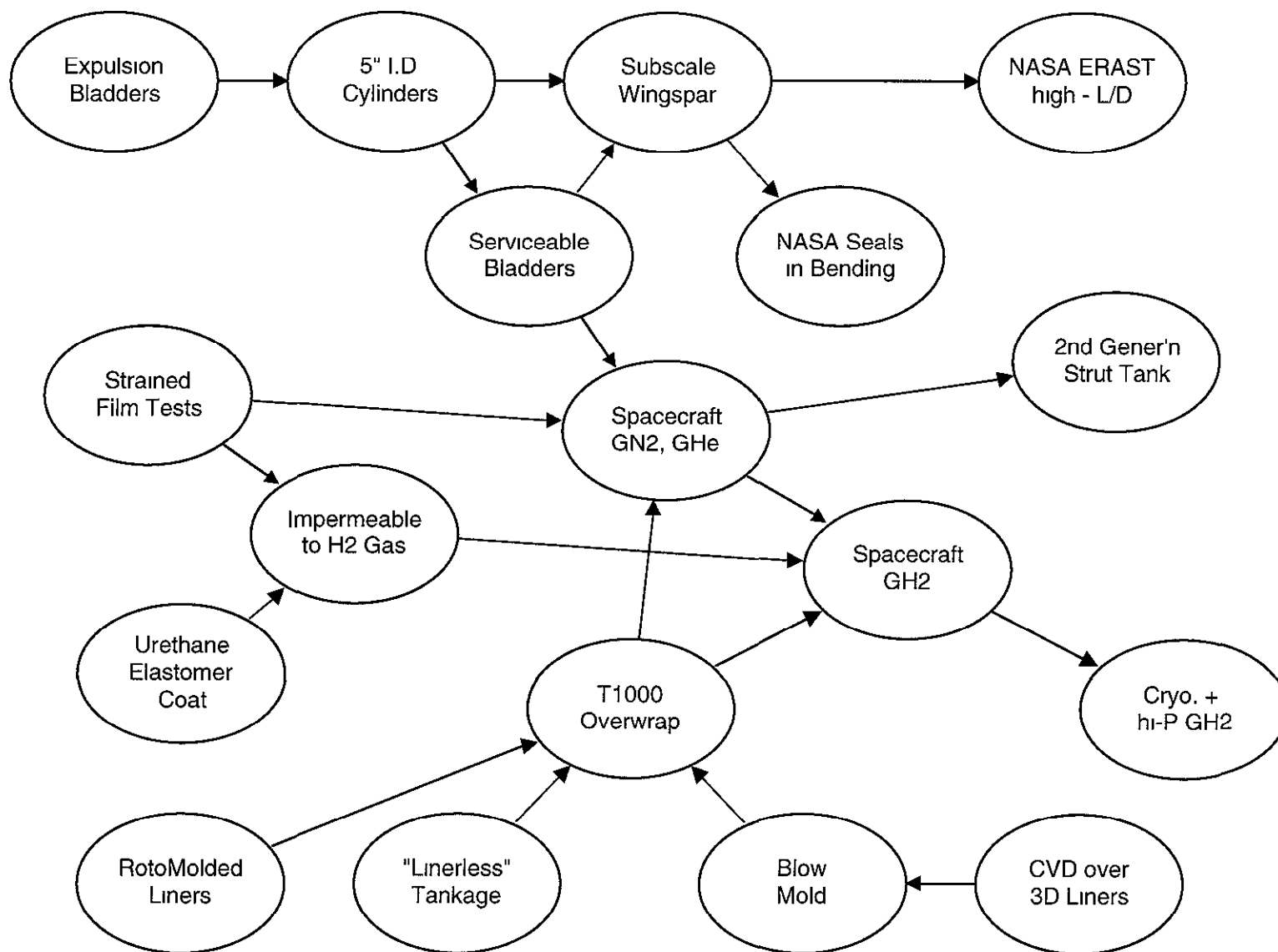


Figure 8

- **Energy storage systems designed for aircraft and automotive applications with >400 Wh/kg packaged specific energy**
- **Primary fuel cell test rig converted into unique test capability**
- **URFC cell tested using H₂/O₂ for more than 2000 cycles between fuel cell and cathode feed electrolysis modes demonstrated less than a few percent cyclic degradation over a range of current densities**
- **Operation at >1000 ASF (>1.1 A/cm²) for URFC in both fuel cell and cathode feed electrolysis modes**
- **Thin tank liners (bladders) fabricated with low-permeability laminates, seamed to thick end domes with bosses molded in place**
- **Thin bladders used as inflatable mandrels to fabricate composite tanks**
- **Prototype composite tanks with estimated performance factors of 1.6 million inches (40 km) have >10% hydrogen storage mass fraction at 300 K**
- **Composite tanks designed with performance factors of 2.0 million inches (50 km) have >12.5% hydrogen storage mass fraction at 300 K**

Figure 18

- **URFC operated in fuel cell mode at 0.6 V to >1000 ASF (>1.1 A/cm²)**
- **URFC test rig upgraded to accomodate anode feed electrolysis in addition to cathode feed electrolysis and fuel cell modes**
- **Rapid cycling (<1 minute cycle between electrolysis and fuel cell) demonstrated, enabling rapid response energy storage applications**
- **Agreements in place to test Hamilton Standard and Proton Energy Systems proprietary hardware on loan to LLNL – preserving ownership**
- **Investigation of high performance membranes initiated with partners**
- **Investigation of reduced catalyst loading for URFC operation underway**
- **New facility capable of wider range of electrochemical, pressure, and contained mass testing is being prepared at LLNL (uncleared white area)**
- **Close collaboration and monitoring of Thiokol under DOE tankage PRDA**
- **Actively interfacing design between Thiokol & DOE/Ford demonstrations**
- **New generation of liner development with Aero Tec Laboratories, Inc.**

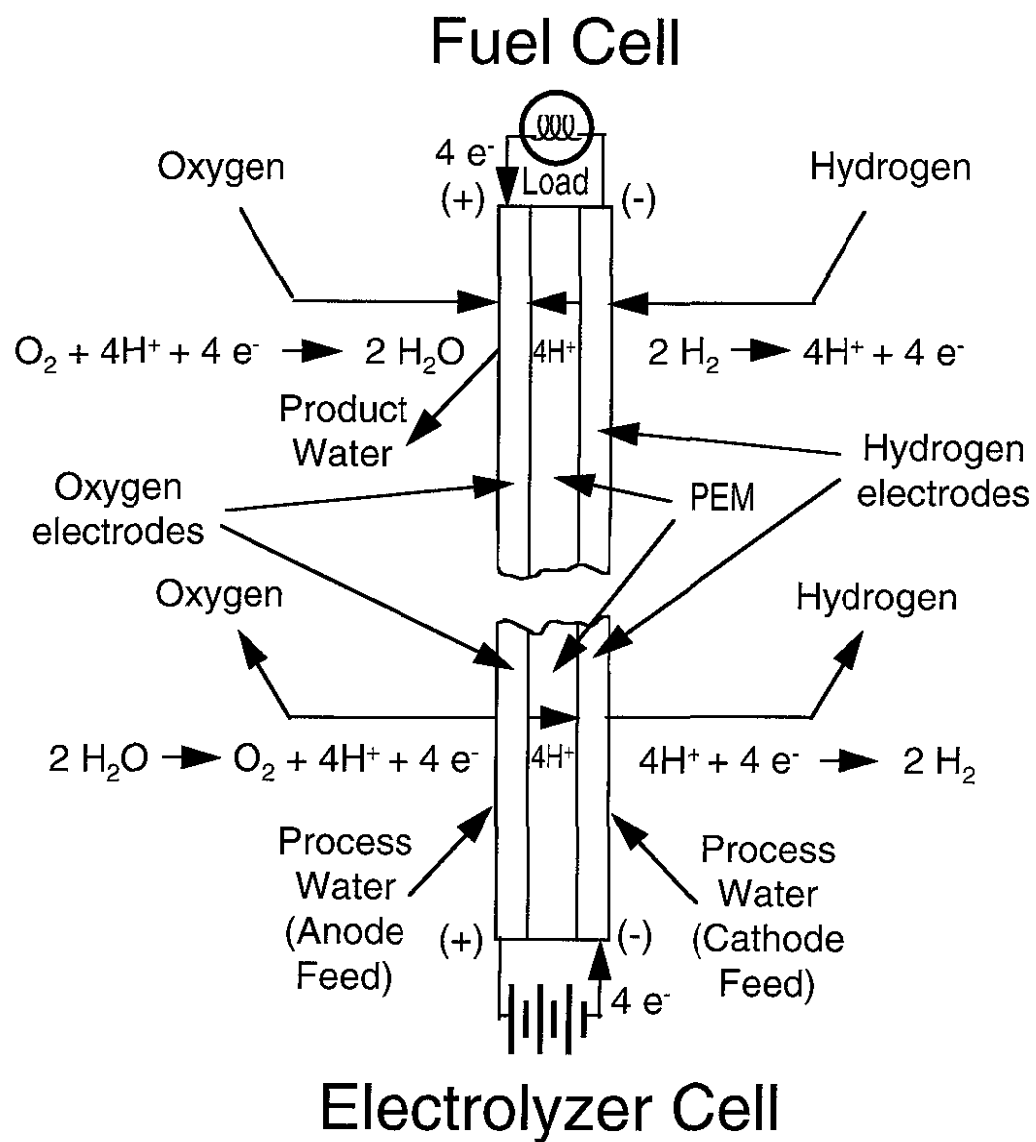
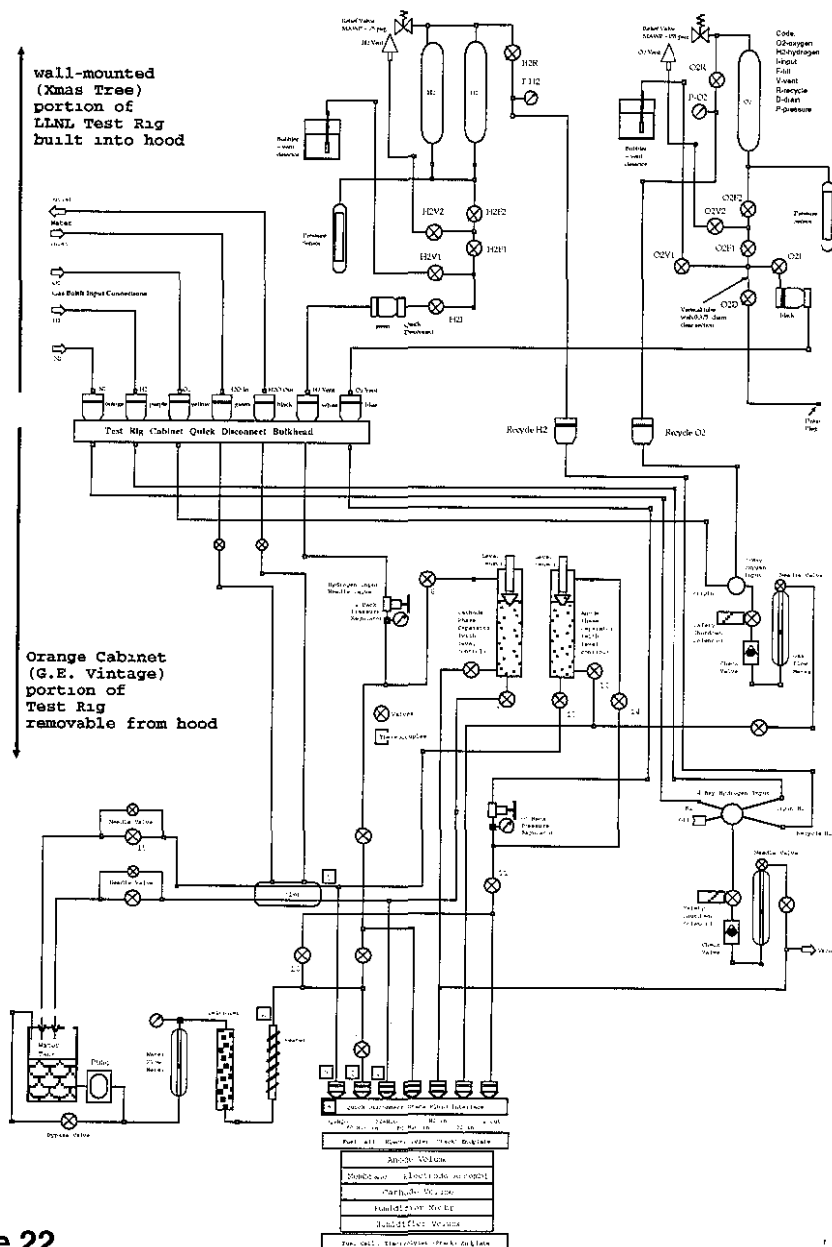


Figure 20



- Able to test cells, stacks, M&E assemblies
- Now able to test both cathode feed and anode feed electrolysis
- Prepared and certified to test with recycled gases (fuel cell operation consuming products of prior electrolysis)
- Allows safe, unattended operation including data logging and multi-mode cycling
- Unique capability to test PEM energy storage systems

Figure 22

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