# LA-UR- 87-2393

Los Alamos National Laboratory is operated by the University of California for the United States Department of Energy under contract W-7405-ENG-36

TITLE FUEL CELLS FOR EXTRATERRESTRIAL AND TERRESTRIAL APPLICATIONS

LA-UR--87-2393

DE87 013160

AUTHOR(S) SUPRAMANIAM SRINIVASAN, (MEE-11)

SUBMITTED TO Symposium on "Electrode Materials and Processes for Energy Conversion and Storage," 171st Meeting of the Electrochemical Society. Philadelphia, PA May 10-15, 1987

#### DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommentation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

By acceptance of this article is e-pool sine recognizes that the U.S. Government relative a numericusive royality-free incense to publish or reproduce the publish of this contribution, or to allow others to do so, for U.S. Government purposes.

The Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy

SALEMOS Los Alamos National Laboratory Los Alamos, New Mexico 87545

# MASTER

F HIM N F B36 N4

#### FUEL CELLS FOR EXTRATERRESTRIAL AND TERRESTRIAL APPLICATIONS

S. Srinivasan Los Alamos National Laboratory Mechanical & Electronic Engineering Division, MSD429 Los Alamos, New Mexico 87545

#### ABSTRACT

The fuel cell is a nineteenth century invention and a twentieth century technology development. Due to the high power and energy density, high efficiency, reliability, and production of pure water, hydrogen-oxygen fuel cell systems have no competition as auxiliary power sources for space vehicles. The alkaline fuel cell system is a well developed and proven technology for this application. The solid polymer electrolyte system may be its future competitor. The energy crisis of 1973 stimulated research, development and demonstration of the phosphoric acid, molten carbonate, solid oxide and solid polymer electrolyte fuel cell systems using natural gas, petroleum or coal derived hydrogen (and carbon monoxide for the high temperature systems) for terrestrial applications. The direct methanol-air fuel cell is still an electrochemist's dream. Though considerable technological advances have been made, the present price of crude oil, and the high capital costs and limited lifetime of fuel cell systems impede their terrestrial applications in the developed countries. Conversely, the potential for lower capital costs of labor intensive manufacturing processes and the relatively higher fossil fuel prices make these systems more attractive for such applications in the developing countries.

# THE FUEL CELLS - A NINETEENTH CENTURY INVENTION AND TWENTIETH CENTURY TECHNOLOGY DEVELOPMENT

Though Sir William Grove discovered fuel cells as early as 1839, it was only in the 1960's that fuel cell system. found their first major application-auxiliary power sources for the Gemini space flights. However, a number of concepts relating to the advantages of converting chemical energy to electrical energy, types of fuels, and temperature ranges for operation

•

The way that

6978R

were alluded to in the research work during the intervening 120 years.<sup>1-3</sup> Though the historical development of fuel cells has been covered adequately in several books and review articles, it is worth summarizing the highlights of the progress made in this period.

- Sir William R. Grove demonstrated the first fuel cell in 1839 by supplying hydrogen to one platinum electrode and oxygen to another with both electrodes contained in sulfuric acid. He connected six of these fuel cells in series and used the electricity generated to decompose water. Platinum is still the best electrocatalyst for aqueous electrolyte fuel cells!
- Becquerel devised a fuel cell in 1855 consuming carbon by immersing it in molten nitre (potassium nitrate) contained in a platinum vessel.
   Platinum also served as the counter electrode. The faradaic efficiency was low because of the direct chemical oxidation of carbon by potassium nitrate.
- Mond and Langer (1889) developed a fuel cell battery in which platinum sheets with many small holes and covered with platinum black ware used as electrodes. Dilute sulfuric acid, retained in a porous plaster-of-Paris matrix, served as the electrolyte.
- Ostwald (1894) recognized the potentially high efficiency of fuel cells,
  i.e., the conversion of the free energy change of a chemical reaction
  directly to electricity.
- Jacques (1897) designed and built a 1.5 kw fuel cell bettery. Each cell consisted of an iron pot containing fused sodium hydroxide into which was placed a carbon rod as the consumable anode.
- The pioneer of the fuel cell era in the twentieth century is Francis T.
  Bacon. He started the development of a hydrogen/oxygen fuel cell battery in 1932. A 5 kw fuel cell power plant was built and tested in 1952. In

2

いいいになって

69788

order to stabalize the gas and electrolyte within the electrodes, these were of a dual porosity construction (Teflon was not discovered at that time). The single cell consisted of a sintered nickel anode, sintered lithiated nickel oxide cathode and 85% KOH. The operating temperatures and pressures were  $200-240^{\circ}C$  and 30 to 40 atm.

 The Bacon fuel call system served as the foundation for the fuel cell power plants (auxiliary power sources) for the Apollo Space Vehicles, developed by Pratt and Whitney Aircraft, Division of United Technologies Corporation.

The energy crisis of 1973 was the impetus for a large number of research and development programs on fuel cell technology for terrestrial applications. The status of fuel cell technologies for extraterrestrial and terrestrial applications is summarized in the next two sections, while the final section deals with the prognosis of economics and applications of fuel cell systems.

Before dealing with these topics, it is worthwhile recollecting some fuel cell principles in respect to systems engineering aspects:

- The fuel determines type of fuel cell and fuel processor.
- The operating temperature determines method of product heat and water removal.
- The application determines power rating, need for bottoming cycle, power conditioning and scale-up considerations.
- Start-up time and peaking capabilities are of primary concern in respect to developing fuel cells for transportation applications.

The heart of the fuel cell system is the electrochemical cell stack. Its basic components are the porous gas diffusion electrodes, electrolyte which may or may not be held in a matrix and the bipolar plate. Their choice design and fabrication procedure is again determined by the primary fuel and by the operating temperature and pressure of the fuel cell power plant.

3

6978B

#### THE SPACE AGE - THE FIRST MAJOR APPLICATION OF FUEL CELL SYSTEMS

The main advantages of fuel cell systems for space applications are high power and energy density with respect to weight and volume, high efficiency, few moving parts, minimum noise and vibration and reliability. For this application, the logical fuel and oxidant are cryogenic hydrogen and oxygen.

The Gemini space flights used a 1 kw General Electric solid polymer electrolyte fuel cell.<sup>4</sup> The distinctive feature of this cell is that a solid electrolyte was used in the form of an ion exchange membrane (polystyrene sulfonate). The two electrodes which consist of the electrocatalyst (finely divided platinum) and a plastic material for wet-proofing the electrode are incorporated on fine metallic (platinum or titanium) wire screens. These electrodes are bonded on both sides of the solid polymer electrolyte. Metallic current collectors are ribbed on to each electrode. The heat removal was by circulating a coolant through tubes in the bipolar current collector to a space radiator. Wicks were used on the cathode side of the current collector to absorb the product water and carry it over by capillary action. The water (1 pint/kwh) was used for drinking purposes by the astronauts.

The Gemini fuel cell system was used for missions of duration about 1-2 weeks. Though it satisfied the performance requirements for such flights, there were some problems with this technology - the power densities attained were not high enough; the polystyrene sulfonate ion exchange membrane electrolyte was not stable under the electrochemical environments in the cell; and, the platinum loading was quite high. Thus, the alkaline fuel cell technology was chosen for the Apollo<sup>5</sup> and space shuttle<sup>6</sup> flights.

The Pratt and Whitney Division of United Technologies Corporation developed alkaline fuel cell systems for the Apollo flights - these fuel cells used the Bacon fuel cell technology with dual porosity electrodes (nickel for the anode and lithiated nickel oxide for the cathode). The dual porosity electrodes served the purpose of stabilizing the electrolyte meniscus within the electrode. Unlike the Bacon fuel cells, these cells used a high concentration potassium hydroxide (80-85% which is practically the molten salt), at a higher temperature (250° rather than 200°C) and close to atmospheric pressure; remarkable improvements in performance have been

Tiutin Citr

reported in futuristic versions of the alkali fuel cell power plants for the space shuttle flights and these are illustrated in Figure 1. The electrodes are Teflon bounded and contain unsupported platinum (anode) and gold-platinum alloy electrocatalysts. The main difference in the electrochemical cell is the use of an extremely thin (50 µm) electrolyte matrix made with potassium titanate. Figure 1 shows that extremely high current densities are achieved in the purely activation controlled region (about 0.5  $A/cm^2$  at 0.9 V), while the slope of the linear region is amazingly low (0.05 ohm cm<sup>2</sup>). This low value of the slope is essential for attaining high current densities (up to 10  $A/cm^2$ ) at moderate cell potentials (0.5 V). The Apollo fuel cell systems (rated power about 2 kW) performed quite satisfactorily for missions which lasted 2-4 weeks. For the space shuttle flights of the 1970's and 1980's, United Technologies Corporation/International Fuel Cells Corporation, developed a high performance alkaline fuel cell system (12 kW), with platinum anodes (10 mg/cm<sup>2</sup> of Pt), and gold (90%) - platinum (10%) cathodes (20 mg/cm<sup>2</sup> of Au-Pt alloy). The electrolyte is 35% KOH and is immobilized in a reconstituted asbestos matrix. An electrolyte reservoir plate is on the anode side to supply electrolyte when needed. The cells operate at about 60-70°C under a few atm pressure. Current densities of about  $1 \text{ A/cm}^2$  at cell potentials of 0.80 V are obtained in these cells. The objectives of NASA are to further improve the performance of these cells by increasing the operating temperature to about 120°C. For this purpose, the gold-platinum electrocatalyst will have to be modified to improve the performance and increase the stability, perhaps by incorporating a third component in the alloy.

A strong competitor for the alkaline fuel cell system is possibly the advanced solid polymer electrolyte fuel cell. Recent results from Siemens, Germany; Ballard Technologies Corporation, Canada; and Los Alamos National Laboratory (LANL), USA, strongly indicate the attainment of high power densities with stable membranes (for example, Nafion and Dow Membranes) and low noble metallic loadings (0.5 mg/cm<sup>2</sup>). Current densities of 5 amp/cm<sup>2</sup> at a cell potential of 0.5 V, 80°C and 8 atm pressure have been reported by Ballard Technologies Corporation and Siemens in solid polymer electrolyte (Dow membrane) fuel cells with Teflon bonded electrodes containing 4 mg/cm<sup>2</sup> unsupported platinum. The reactants are pure H<sub>2</sub> and O<sub>2</sub>. The Los Alamos

5

Thursday DiviFT

National Laboratory investigators are focussing on achieving high power densities in such fuel cells using low noble platinum loading electrodes. The manner in which this is achieved is by impregnation of a proton conductor (e.g., Nafion) into a "conventional" porous gas diffusion electrode used with liquid electrolytes. The rationale for this approach is that the reaction zone for a fuel cell reaction at a solid electrode/solid electrolyte interface is close to a "three phase line." Impregnation of the proton conductor into the electrode structure considerably extends the three phase zone and approaches that in the case of a liquid electrolyte. Current densities of 1  $A/cm^2$  have been attained at cell potentials of 0.5 V. The slopes of the linear region in the cell potential-current density plots are 0.1 and 0.2 ohm cm<sup>2</sup> for the Ballard Technologies Corporation and LANL single cells, respectively. The main reason for the lower slope, which is central for attainment of higher current densities appears to be the use of the Dow membrane in the former and the Nafion membrane in the latter case. The Dow membrane used by Ballard Technologies Corporation has a smaller thickness (125 vs 175µm), higher acidity and better water retention characteristics than the Nafion membrane used in the LANL single cells. The Ballard fuel cells were also operated at a higher pressure (8 vs 5 atm) than the LANL ones.

# THE ENERGY CRISES OF 1973 - A RENAISSANCE OF FUEL CELL TECHNOLOGY FOR TERRESTRIAL APPLICATIONS

The NASA R&D programs on fuel cell technologies initiated in the 1950's, stimulated similar programs in the USA and several European countries during this and succeeding decade for terrestrial applications. Considerable efforts were made to use fuels such as natural gas, the higher hydrocarbons, methanol, ethanol and other organic fuels, directly in fuel cells.<sup>1</sup> In the latter part of the 1960's, the interest faded away because of the low efficiency and power density achieved in fuel cells which use organic fuels directly as the anodic reactant. United Technologies Corporation (UTC), with their strong "forte" in alkaline fuel cell technology for extraterrestrial applications, also provided leadership in the development of fuel cells for terrestrial applications. Even prior to the energy crisis of 1973, UTC embarked on a program with some support from electric and gas utilities to develop fuel cell

6

The All City

power plants utilizing natural gas. Such types of fuel cell power plants were being considered as substitutes for gas turbines which were and still are being used as peaking devices in electric utility power plants.

The energy crisis of 1973 was the "rationale" for renaissance of fuel cell technology for terrestrial applications.<sup>3</sup> The Energy Research and Development Administration (ERDA which subsequently became the U. S. Department of Energy) and the Electric Power Research Institute (EPRI) stressed the need for conservation of the petroleum fuels and for the increasing utilization of coal, natural gas, and renewable energy resources. The potential benefits of fuel cell power plants for peak shaving, load following and intermediate and base load power generation in electric utility applications are:

- The chemical energy of a fuel is directly transformed into electricity. Thus, the theoretical efficiency is not limited by the Carnot cycle as is the case for conventional thermal power plants.
- Fuel cell power plant efficiencies are independent of the rated power above say about 100 KW. This is not so with oil or coal burning power plants, gas turbines, and diesel generators, where the efficiency is reasonably constant only at the megawatt power level.
- Fuel cells can be made in a variety of sizes and they are modular. This permits locating such power plants at several grid systems to reduce transmission line costs. This advantage is particularly important in congested urban centers, where the needed transmission and distribution facilities are expensive to install;
- The siting advantages of fuel cell power plants can be extended because of their capabilities for waste heat utilization (as for example, space heating, hot water, and absorption cooling). The combined efficiency for electricity and heat production can be as high as 90%. This is quite attractive for gas utilities having extensive gas distribution systems

7

Tiucin Differ

• Fuel cell power plants make a lot of sense for installation in large industries which need both electricity and high grade heat.

In the late 1970's, programs were initiated at Brookhaven National Laboratory and Los Alamos National Laboratory for the investigation of fuel cell power plants for vehicular power plants.<sup>9</sup> Some of the above advantages of fuel cell power plants over thermal ones for electric and gas utility power generation apply equally well for vehicular power plants. The significant one is that the projected efficiencies for fuel cell power plants are at least twice as high as internal combustion and diesel engines.

In the 1970's, it was realized that because activation overpotentials for anodic oxidation of organic fuels are too high and poisoning problems by their intermediates are ercountered, it is necessary to process these fuels to hydrogen prior to entry into the electrochemical cell stack. In the high temperature fuel cell systems, carbon monoxide is also an efficient anodic reactant. Natural gas and coal are the primary fuels of most interest for terrestrial applications of fuel cells. Methanol, a liquid fuel which is mass produced from natural gas and in the future possibly from coal, is another attractive fuel, particularly for transportation applications. This fuel is the most electroactive organic fuel but its activity is about three orders less than that of hydrogen. Thus, at the present time, even methanol will have to be steam-reformed to hydrogen before entry into the anode gas chamber. The processing of organic fuels restricts electrolytes to carbon dioxide rejecting ones - phosphoric acid, molten carbonate, solid oxide, and solid polymer electrolyte (the last is with processed methanol as fuel). The following subsections briefly describe the status of each of these technologies. For more details, the reader is referred to recent publications. 3,10

<u>Phosphoric Acid Fuel Cell Systems</u>: Apart from the alkaline fuel cell systems for space applications, this technology is the most advanced. Systems ranging from 1 kW to 5 MW have been designed, built and tested. The most advanced version operates at 205°C, 8 atm pressure, at a current density of 325  $mA/cm^2$  and 0.7 V/cell. The noble metal loading of the anode is 0.25 mg/cm<sup>2</sup>

8

and of the cathode is 0.5 mg/cm<sup>2</sup>. Some platinum alloy electrocatalysts (with Cr, V) show improved performance but lifetime is a problem. These systems are being considered for load following in electric utilities and on site integration energy systems. The chemical  $\rightarrow$  electrical energy conversion efficiency at the rated power level is about 40% and chemical  $\rightarrow$ (electrical & heat) energy conversion efficiency is over 80%. Lifetimes of over 5 years have been attained on demonstration systems.

The materials used for the fabrication of components in a phosphoric acid fuel cell are shown in Fig. 2. The anode and cathode consist of porous gas diffusion electrodes. These electrodes can be prepared by one of three methods. The spraying method (Fig. 3), many steps of which can be automated, is the most commonly used. Filtration and rolling methods are also used. The former is good for preparing experimental electrodes for research purposes. The rolling method is somewhat tedious, but result in electrodes which are reproducible from the point of view of electrochemical performance. The silicon carbide matrix (about 50-100 µm thick) is generally deposited on top of an electrode (say, cathode) by a wet process which involves preparation of a silicon carbide - Teflon emulsion and spraying or continuous feeding to the electrode. The purpose of the small quantity of Teflon is to serve as a binder. The electrode-silicon carbide assembly is then heated to dry the matrix and sinter the Teflon in it. The porous carbon serves three purposes it is grooved to permit gas distribution; in the United Technologies Corporation design it serves as an electrolyte reservoir; and it is a current collector.

The active layer in the electrode consists of platinum supported on carbon and Teflon. The Teflon content in the layer is about 40%. Platinum crystallites are deposited on the high surface area carbon generally by a colleidal method followed by heat pretreatment. The aim is to have platinum crystallites with a diameter of about 50 Ű. An electron microscope photograph of the supported electrocatalysts is shown in Fig. 4. One of the performed degradation mechanisms in fuel cells electrodes is the agglomeration or sintering of platinum crystallites, causing loss of electrochemically active surface area. It is generally accepted at the present time that this phenomenon is due to surface migration of platinum

9

ていいいていた

6978B

crystallites, followed by their coalescence. The low temperature sintering is significantly influenced by the electrolyte. Another cause for performance degradation is poisoning of mainly the anode. Poisons which can be encountered are CO and  $H_2S$  from reformed fuels, organic impurities in cell component materials and metallic impurities, from say cooling pipes.

Plans are underway to build 11 and 7 1/2 MW phosphoric acid fuel cell power plants by International Fuel Cells Corporation (a division of United Technologies Corporation) and Westinghouse Corporation. Figure 5, a schematic of the former one, demonstrates that the electrochemical cell stack is a small but vital component of the entire system. These power plants are being considered for "load followers" by the electric utilities. Such types of power plants are being strongly identified in Japan for the stated and dispersed power generation applications. Toshiba is in International Fuel Cells Corporation for the development and installation of these types of power plants.

Molten Carbonate Fuel Cell Systems: This is an ideal system to be used with reformed natural gas and gasified coal. Progress has recently been made at Energy Research Corporation for the internal reforming of natural gas (i.e., with catalyst system ahead of the anode). This eliminates a major component the fuel processor. Carbon monoxide produced from natural gas or coal is a reactant and not a poison for the molten carbonate full cell system unlike in the phosphoric acid fuel cell system. The components of the single cell in a molten carbonate fuel cell are represented in Fig. 6. The electrolyte (lithium and potassium carbonate) is held in a tile (lithium aluminate). The anode is made of porous nickel and the cathode of porous nickel oxide. The reactions in a molten carbonate fuel cell are depicted in Fig. 7. The cathode material is transformed into lithiated nickel oxide by its interaction with the electrolyte. Lithiated nickel oxide is a better electronic conductor and also more corrosion resistant than nickel oxide. However, corrosion of the cathode material is one of the most serious problems in this fuel cell. Use of Ni-Cr or Ni-Cu alloys inhibits the sintering of the Ni and the presence of Cr reduces the sulfur poisoning. Attempts are being made to find spinels and perovskites as substitutes for the lithiated nickel oxide cathodes which tend

- Civin CiviFI

6978E

10

to corrode slowly in the electrolyte. The bipolar plate consists of two layers - nickel on the hydrogen side and stainless steel on the oxygen side. The morphology and porosity of each of the cell components is shown in Fig. 8. The pores in the electrolyte tile are relatively small compared to those in the electrodes. Activation overpotential losses are minimum in this cell. The cell potential - current density relation is linear (Fig. 9) and the cells are designed to operate at 0.7 V and 150 mA/cm<sup>2</sup>. The slope of this line is about four times as high as in the linear region of the same plot for the phosphoric acid fuel cell system. High grade heat, liberated by this system, can be used for electricity generation in a gas turbine or used as such by chemical industry. Efficiencies for electricity generation as high as 60% are projected.

Molten carbonate fuel cell programs are ongoing in the U.S.A., Japan, and Italy. Fuel cell powerplants with an electrode area of 1/2 to 2 m<sup>2</sup> are planned to be built. The multicell stack will consist of 75 to 700 cells. Each of these will deliver a power output of 5 KW to 1 MW. International Fuel Cells Corporation is the forerunner for the development of molten carbonate fuel cells. There are two lines of approach. One is to build a stack with electrode area of 0.1 m<sup>2</sup> and the other with that of 0.8 m<sup>2</sup>. The areas of active research are (i) improved electrolyte management, (ii) stabilization of cathode, (iii) reduction of anode compaction and low cell to end plate rewistance; and (iv) examination of effects of H<sub>2</sub> S on moltan carbonate fuel cell performance.

<u>Solid Electrolyte Fuel Cell Systems</u>: The rationale for developing solid electrolyte fuel cell systems is its high projected efficiency for electricity generation, by using gasified coal, as compared with those of the phosphoric acid and molten carbonate fuel cells. A schematic of a solid electrolyte fuel cell power plant is shown in Fig. 10. In recent years, attention has been focussed on natural gas, instead of coal as the primary fuel. This is because of the vast proven reserves of this fuel in many countries including the U.S.A. It is also simpler to process natural gas than coal to the fuel cell fuels (H<sub>2</sub> and CO). The processed fuel enters the electrochemical cell stack where the chemical energy of the fuel is transformed to electricity. This

11

いいいいたが

fuel cell with the yttria stabilized zirconia (12% yttria in zirconia) electrolyte operates at 1000°C. The high quality waste heat enters the steam generator which in turn supplies steam to the steam turbine to produce more electricity. The total efficiency for the production of electrical energy from the chemical energy of coal or natural gas using the fuel cell system and the gas turbine is projected to exceed 60%.

Rapid advances in this technology have been made at Westinghouse Corporation during the last 5 years. This is in respect to a tubular design (closed at one end) with connections of cells in series and parallel. Layers of the cathode, electrolyte and anode material are deposited on the closed end porous zirconia tube (see Fig. 11) by chemical or electrochemical vapor deposition techniques. The cathode of one cell is connected to the anode of the next cell by a strip of interconnection and nickel felt. Two cells are connected in parallel with a nickel felt. The series - parallel connection in four cells is represented in Fig. 12. The nickel felt is in a reducing environment and is stable. Nickel is the anode electrocatalyst and strontium doped lanthanum manganite the cathode electrocatalyst. Magnesium doped lanthanum chromite is the material used for the interconnection. The operating temperature is 1000°C. The cell potential-current density relation is linear. The slope is relatively high - about 0.60 ohm/cm<sup>2</sup>. Thus, the current density at about 0.65 V is about 150 mA/cm<sup>2</sup>. The improvement in performance of oxygen over air, as seen in Fig. 13, is due to thermodynamic, electrode kinetic and "barrier layers" effects. The H\_/sir fuel cell performance can be improved by minimizing the "barrier layer" effect, i.e., reducing the thicknesses of the support tubes, and of the cathode layer as well as increasing the porosity.

The power versus current or current density plot is also shown in Fig. 13. Each tube has a designed power output of 18 watts. The cell performance is stable over several hundred hours. This led to the design, engineering and construction of multicell stacks. A fuel cell bundle consists of twelve tubular cells, arranged in a three-parallel by four series matrix. A series connection of two bundles is made at one side and power terminals are connected to each of the bundles on the other side. Thus, the twenty-four cells exhibit eight times the voltage and three times the current of a single cell. 12 6978E

The generator which consists of the twenty-four cell stacks also has a thermal insulation package. The latter includes the cell-support structure and gas distribution systems. The temperature distribution within the cell bundle is maintained only by waste heat generation from the fuel cells and combustion of the spent gases in the exhaust chamber (15% of supplied fuel). Heat exchange in the spent fuel combustor preheats the inlet air supply and limits the exhaust gas temperature.

The successful design, construction, and performance evaluation of the 24-cell stack led to the construction of a 5 KW fuel cell generator. This multicell stack consists of 324 single cells. The sub-cell stacks, consisting of the 24 cells, are connected in series to form the multi-cell stack. Performance evaluation of the 5 KW fuel cell system is now in progress. Like in the molten carbonate fuel cell system, hydrogen and carbon monoxide may be used as processed fuels. Again, because of the high grade heat, it is designed to generate more electricity in a bottoming cycle or be used as such for cogeneration applications. Efficiencies for electricity generation will be higher than that for the molten carbonate system.

Solid Polymer Electrolyte Fuel Cell Systems: This system is being considered for transportation applications. Since the system operates at less than  $100^{\circ}$ C, methanol is the most appropriate liquid fuel to be reformed and used in this fuel cell system. As stated in the preceding section, progress had been made at Los Alamos National Laboratory to reduce the noble metal loading to one tenth that in the state-of-the-art system developed by General Electric Company/Hamilton Standards. This is done by incorporating a proton conductor into the electrode structure to extend the three dimensional reactor zone. The water management in the system can be achieved by optimum humidification of the system. Prospects are good for attaining high power densities - over 500 mW/cm<sup>2</sup>.

<u>Direct Methanol Fuel Cell</u>: A fuel Cell Researcher's Dream: A fuel cell researcher's dream is to oxidise organic fuels (preferably methanol which is easily produced from natural gas or coal) rather than process these to hydrogen, which is in turn oxidised to hydrogen in the electrochemical cell.

13

T. J. J. L. L. L.

Methanol is the most active electroorganic fuel but its activity in three orders of magnitude less than that of hydrogen. Thus, under these conditions current-densities of about 50 mA/cm<sup>2</sup> are obtained at cell potentials of 0.4 V. Even at these current densities, there is a performance degradation with time. The main cause for it is that the intermediates formed during methanol oxidation poison the platinum electrocatalyst. The poisoning effects are less with some alloy electrocatalysts (e.g, Pt-Ru, Pt-Sn) and platinum electrocatalysts with ad atoms (Bi, Pb, Sn, Ge). The probable mechanisms for inhibition by such electrocatalysts is that the second elements is either in an oxidised state which catalyzes the oxidation of the organic intermediates or an inhibitor for hydrogen adsorption on platinum, thereby preventing the formation of a hydrogenated organic inhibitor.

Attempts have been made to oxidise methanol in a phosphoric acid fuel cell at elevated temperatures (say 200°C). In this case, methanol was fed as a vapor into the cell. The main problem was that unreacted methanol migrated from the anode to the cathode where it acted as a depolarizer for the oxygen reduction reaction.

#### PROGNOSIS OF ECONOMICS AND APPLICATIONS OF FUEL CELL SYSTEMS

The applications of fuel cell systems have been well demonstrated in space vehicles. Capital costs are not such an overriding factor for space applications as for terrestrial applications. The alkaline and possibly the solid polymer electrolyte fuel cell systems will continue to be the auxiliary power sources for space vehicles. Regenerative fuel cells will have to be developed for long space flights (more than a few months) and space laboratories.

The present price of crude oil makes it more difficult for the entry of fuel cell systems into the terrestrial arena particularly in the developed countries. Fuel cells may find nearer term applications in the developing countries, particularly for dispersed power generation using biomass fuels (biogas, alcohols). Since the manufacturing processes for fuel cells are labor intensive, the capital costs of these systems could be considerably lower in the developing countries. Further, the cost of fuels in these countries are realistically and relatively (in respect to per capita income) higher in the developing countries. Thus, the need for fuel cell technology

14

6978K

is higher in the developing countries. In the developed countries, fuel cell technologies can make an impact on-site integrated energy and cogeneration applications. Environmental constraints can also accelerate the entry of fuel cell technologies.

The bottom line with respect to economics of fuel cells for terrestrial applications, will be the cost of electricity generated, which in turn will depend on capital costs, efficiency and lifetime.Taking into consideration the performances of the four types of fuel cells for terrestrial applications, the major factors to be overcome are: (i) develop automated techniques to reduce the capital costs of the system to about \$1000-\$2000/kW (high capital cost at the kW level and lower at the MW level) for stationary applications and \$200/kW for transportation applications; (ii) achieve reliability of performance c er the required lifetimes; (iii) demonstrate economic, technical and environmental advantages of dispersed, on-site integrated energy and cogeneration power plants; and (iv) find niche for electric vehicles - in plant, military, buses, trucks, and automobiles?

The factors which impede the commercialization of fuel cells are:

- Capital cost, operating cost, lifetime, reliability, weight, and volume.
- Capital costs and power/weight and power/volume which are primarily dependent on power density.
- Operating costs which are determined by amortization of capital costs (hence lifetime) and efficiency.
- Material costs of fuel cell components which are relatively low except for the solid polymer electrolyte fuel cell system.

15

 Capital costs which are relatively high because manufacturing costs are labor intensive.



6978K

- For fuel cell systems to have an efficiency greater than 50%, single cell potential must be greater than 0.75 V (i.e., half the thermoneutral potential for the reaction  $H_2 + 1/2 = 0_2 \rightarrow H_2^0$ which is 1.48 V.
- Open circuit potential for all fuel cells is approximately 1.0 V. To attain high current densities with this open circuit potential and cell potential of 0.75 V, the slope (dE/di) in the linear region of the cell potential versus current density plot has to be small, say about 0.1 ohm cm<sup>2</sup>. The lowest values of (dE/di) reported for the five types of fuel cell systems are found in Table I. It can be readily seen from this table that the only fuel cell systems which can attain high current densities are the ones with alkaline and solid polymer electrolyte. The phosphoric acid fuel cell system is considerably closer to attaining higher current densities than the molten carbonate or solid electrolyte fuel cell systems because of the respective (dE/di) values.

#### ACKNOWLEDGEMENTS

This work was carried out under the auspices of the U. S. Department of Energy. The author wises to thank Dr. Jack T. Brown of Westinghouse Corporation for lending the slide material on solid oxide electrolyte fuel cells, which were quite valuable for the preparation and presentation of this paper.

#### REFERENCES

- J.O'M. Bockris, and S. Srinivasan, Fuel Cells: Their Electrochemistry, McGraw Hill Publishing Company, New York (1969).
- 2. K. V. Kordesch, J. Blectrochem. Soc., 125, 77C (1978).
- 3. S. S. Penner, Ed., Assessment of Research Needs for Advanced Fuel Cells.

16



6978K

- 4. H. T. R. Maget, Chapter II in C. Berger, Ed., Handbook of Fuel Cell Technology, Prentice Hall, Inc., Englewood Cliffs, NJ (1968).
- 5. C. C. Morrill, Proc. Ann. Power Sources Conf., 19, 38 (1965).
- 6.
- I. D. Raistrick, Proceedings of the Symposium on Diaphragms, Separators and Ion Exchange Membranes, 86-13, 172 Electrochemical Society, Inc., Princeton, NJ (1986).
- 8. S. Srinivasan, E. A. Ticianelli, C. R. Derouin, and A. Redondo, J. Power Sources. In Press.
- B. A. Ticianelli, W. Paik, C. R. Derouin, I. D. Raistrick, A. Redondo, and S. Srinivasan, Extd. Abs., 171st Meeting of the Electrochemical Society, Honolulu, Hawaii, October 18-23, 1987. In Press.
- 10. P. Stonehart, B. D. McNicol, E. J. Taylor, and S. Srinivasan, Chapter 8 in B. D. McNicol and D. A. J. Rand, Eds., Power Sources for Electric Vehicles, Elsvier, Amsterdam (1984).
- 11. Fuel Cells: Technology Status Report, Morgantown Energy Technology Center, U. S. Department of Energy, Report #DOE/METC-86-0241 (DE 86006619), Morgantown, West Virginia (1985).

## TABLE I

## Lowest Values of Slopes of Linear Regions of Cell Potential-Current Density Plots (dE/di) Reported for the Five Types of Fuel Cells

Type of Fuel Cells	<u>(dE/di), ohm cm<sup>2</sup></u>
Alkaline	0-05
Solid Polymer	0-10
Phosphoric Acid	0-20
Molten Carbonate	0-80
Solid Electrolyte	0-65



.



Porous conductive graphite layer

ANODE Porous Pt supported on carbon with a Teflon binder

ELECTROLYTE H<sub>2</sub>PO<sub>4</sub> in an inert silicon-based matrix

CATHODE. Porous. Pt supported on carbon with a Teffon binder

Porous conductive graphite layer





Eng. 2







Rucher LiverT



A 3 (527

# **MOLTEN CARBONATE FUEL CELL CONSTRUCTION MATERIALS**





Lucius Livit



ANODE Nichel-Chromium

2 pm

CATHOPE Lithiated Nickel Cuide

method with carbonale salth

MICROGRAPHS OF MOLTEN CARBONATE FUEL CELL ELECTHODES AND ELECTROLYTE SUPPORT

ELECTROLYTE PPORT

LINIO2

MOLTEN CARBONATE FUEL CELI. ELECTRODE AND ELECTROLYTE PLATES

Fr. ?



•

Coll performances in V) are plotted to coll current density for colls using tiles fabricated by various techniques. The colls operated at 656 °C: 75% of the fuel gas (62% H<sub>2</sub>, 11% CO, 7% CO<sub>2</sub>, 29% H<sub>2</sub>O) use utilized and 50% of the oxident gas (75% air, 25% CO<sub>2</sub>) use utilized. <sup>33</sup>





FOULLI DINT

- .





Component	The knew (cm)	Materiai	Fabrication Process
Support Tube	01	Calcia-Stabilized Zirconia	Extrusion Sintering
Air Electrode (Cathode)	0.07	Modified Lanthanum Manganite	Slurry Coat/Sinter
Solid Electrolyte	0.001	Yttria-Stabilized Zirconia	EVD•
Interconnection	0.004	Modified Lanthanum Chromite	EVD•
Fuel Electrode (Anode)	0.001	Nickel-Zirconia Cermet or Cobalt-Zirconia Cermet	Slurry Coal/Sinter

TABLE 1. Solid Oxide Fuel Cell – Summary of Components, Component Thicknesses, Materials, and Fabrication Processes .

\* Electrochemical vapor deposition



### CELL-TO-CELL CONNECTION IN THE SOLID OXIDE FUEL CELL



ר' - נ'



ILUCCH LIVIT

S.,13