



CORPORATE RESEARCH AND DEVELOPMENT • SCHENECTADY, NEW YORK

## **ELECTROCHEMICAL ENERGY STORAGE AND CONVERSION**

by

Browall, KW  
Inorganic Materials and Structures Laboratory

TECHNICAL INFORMATION SERIES

1

CLASS

Report No. 81GRD258

November 1981

---

**GENERAL  ELECTRIC**



# TECHNICAL INFORMATION SERIES

<b>AUTHOR</b>  <b>Browall, KW</b>	<b>SUBJECT</b>  <b>Electrochemistry</b>	<b>NO.</b> 81CRD258 <b>DATE</b> November 1981
<b>TITLE</b>  <b>Electrochemical Energy Storage and Conversion</b>		<b>GE CLASS</b> 1 <b>NO. PAGES</b> 12
<b>ORIGINATING COMPONENT</b> Inorganic Materials and Structures Laboratory		<b>CORPORATE RESEARCH AND DEVELOPMENT</b> SCHENECTADY, N.Y.
<b>SUMMARY</b>  <p>Although electrochemical cells for storing and generating electricity have been studied for 200 years, only in the last 20 years has there been significant interest and progress in developing electrochemical technologies for large-scale applications such as electric utility power generation and storage. This interest is a direct result of the rapidly increasing cost and decreasing availability of conventional fuels and the high conversion efficiency of electrochemical devices. Two technologies under development by General Electric are discussed in detail. These are Beta Batteries for electric utility energy storage and electric vehicle applications and Carbonate Fuel Cells for utility power generation. The challenges and status of these two electrochemical technologies are discussed.</p>		
<b>KEY WORDS</b>  <b>Batteries, Beta Battery, Sodium-Sulfur Battery, Beta-Alumina, Solid Electrolyte Fuel Cells, Carbonate Fuel Cell Power Generation, Energy Storage</b>		

INFORMATION PREPARED FOR \_\_\_\_\_

# ELECTROCHEMICAL ENERGY STORAGE AND CONVERSION

K.W. Browall

## 1. INTRODUCTION

Electrochemical cells for producing and storing of electricity have been studied for nearly 200 years. Until very recently, development centered on cells to meet specialized, small, premium-value applications requiring portable power — ranging from flashlight batteries to aerospace fuel cells. In the last 20 years, rapidly increasing attention has been focused on larger scale electrochemical cells for energy conversion and storage, for applications such as electric utility power and electric vehicles. The driving force toward these new applications is the combination of high energy conversion efficiency and storage capability; these features are now beginning to overcome the capital cost and durability drawbacks of earlier electrochemical cells.

The trade-off between fuel cost and capital cost for competing technologies has taken on new importance as a result of rapidly increasing energy prices. For example, the fuel-to-electricity efficiency of a typical gas turbine used by utilities for peak power generation is about 25-30%, and older units are even less efficient. Gasoline engines for automobiles have a similar efficiency, at best. Furthermore, these devices use premium, high-cost fuels. On the other hand, turbines and gasoline engines are relatively cheap, on the order of \$200/kW for a gas turbine. The steep fuel price increases over the last ten years have made electrochemical power generation, with fuel-to-electricity efficiencies on the order of 50%, potentially competitive. Similarly, full-cycle electrochemical storage efficiencies can be on the order of 80%, making utility load-leveling potentially attractive. Yet, even with these high efficiencies, high capital costs (\$900/kW for a coal-fired fuel cell system) make many new technologies difficult to justify.

Clearly, then, the decision to develop advanced energy technology cannot rest with the technologist alone. In terms of relevance to the electrochemical energy conversion and storage technologies, where high capital costs are a concern, the technologist must be driven toward only those systems which can *conceivably* be made inexpensive; this usually translates to cell couples for which reactants, catalysts, and other materials of construction are abun-

dant and cheap and likely to remain so. Finally, there are political and strategic considerations; for example, the value of substituting coal for natural gas is not fully measurable in terms of dollars. The two advanced electrochemical systems to be discussed in this paper — the Beta Battery and the Carbonate Fuel Cell — appear to fulfil all of the technical, economic, and strategic requirements for a commercial system. Both concepts have been under development at General Electric\* for several years. The applications, technical challenges and progress for these systems will be discussed.

## 2. THE BETA BATTERY FOR ENERGY STORAGE

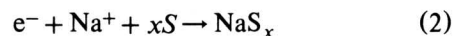
### 2.1 The Beta Cell

The "Beta Cell" derives its name from the unique solid electrolyte separator, a sodium-ion conducting material called sodium-beta-alumina. The discovery of sodium-ion conduction in this material by Weber and Kummer<sup>1</sup> in 1967 opened the possibility of several electrochemical cell couples which might have rapid electrode kinetics if liquid phase electrodes were used. From reactant considerations such as cost, availability, and melting point and electrochemical considerations such as cell potential and energy density, sodium (m.p. 98°C) and sulfur (m.p. 113°C) were selected as the most promising couple.

During cell discharge sodium is oxidized at the cell anode (negative electrode) via the half-cell reaction,



Sodium ions are transported through the beta-alumina, where they reduce sulfur at the cell cathode, according to the half-cell reaction,



Electrons flow through an external circuit to produce dc power. The sulfur electrode chemistry is

\* These programs have been supported, in part, by the United States Department of Energy, the Electric Power Research Institute, Gas Research Institute, and New York State ERDA, as well as by the General Electric Co. Support by these organizations is gratefully acknowledged.

somewhat complicated because sodium and sulfur form a range of product stoichiometries with the initial reaction product  $\text{Na}_2\text{S}_5$ , corresponding to an open circuit potential of 2.08 V, followed by  $\text{Na}_2\text{S}_3$  product, corresponding to an open circuit potential of 1.78 V, and finally to  $\text{Na}_2\text{S}_2$ . All of the polysulfides  $\text{Na}_2\text{S}_x$  with  $x \geq 3$  melt below 300 °C, but  $\text{Na}_2\text{S}_2$  melts at 475 °C. At the temperature of cell operation, 300-350 °C, sulfur and  $\text{Na}_2\text{S}_5$  are immiscible liquids such that this "two phase region" serves to fix the cell open circuit potential at 2.08 V; as the reaction proceeds further, liquid  $\text{Na}_2\text{S}_3$  forms, so that when all sulfur and  $\text{Na}_2\text{S}_5$  have reacted, the cell potential drops to 1.78 V. Since further discharge would result in irreversible precipitation of solid  $\text{Na}_2\text{S}_2$  the drop in cell potential to 1.78 V serves as a convenient "end of discharge" warning. The Beta Battery is a secondary battery, meaning that the above reaction sequence is reversible, and the cell can be recharged by applying the appropriate dc potential.

Several other cell components are necessary for the effective functioning of the cell. The laboratory cell shown in Figure 1 employs a "central sodium" electrode; since sodium is a good electronic conductor, no additional current collector other than the mild steel sodium container is needed. The sodium is contained in a tubular-shaped polycrystalline sintered beta-alumina solid electrolyte; in addition to the obvious requirement of chemical stability toward the reactants and products, the solid electrolyte should be resistant to thermal or mechanical stresses, have good sodium-ion conductivity, and virtually no electronic conductivity. The electrolyte tube is sealed with a glass to an  $\alpha\text{-Al}_2\text{O}_3$  insulator, which electrically separates the two electrodes. The  $\alpha\text{-Al}_2\text{O}_3$  insulator is, in turn, sealed to the respective container halves by diffusion bonding. Since the sulfur electrode is poorly conducting, graphite felt is interspersed to provide electronic conduction and current collection, and to make contact with the mild steel sulfur container. Because of the highly corrosive nature of the sulfur/sodium polysulfide electrode, a GE-proprietary process is used to apply a chromium coating on the steel container.

Laboratory cells are typically discharged at  $\sim 1.9$  V and at a constant current of  $110\text{mA}/\text{cm}^2$  of electrolyte area. Discharge, normally using 75% of theoretical capacity, is carried out over a five-hour period. When the cell discharge voltage reaches 1.7 V, end-of-discharge is indicated, as discussed above. Charging takes place at  $\sim 2.3$  V over a

seven-hour period. Figure 2 shows typical charge-discharge behavior. Laboratory cells are cycled continuously to provide the maximum number of cycles in the minimum amount of time; the charge/discharge profile of full-size cells in actual commercial applications would be similar, but cycling would not likely be continuous.

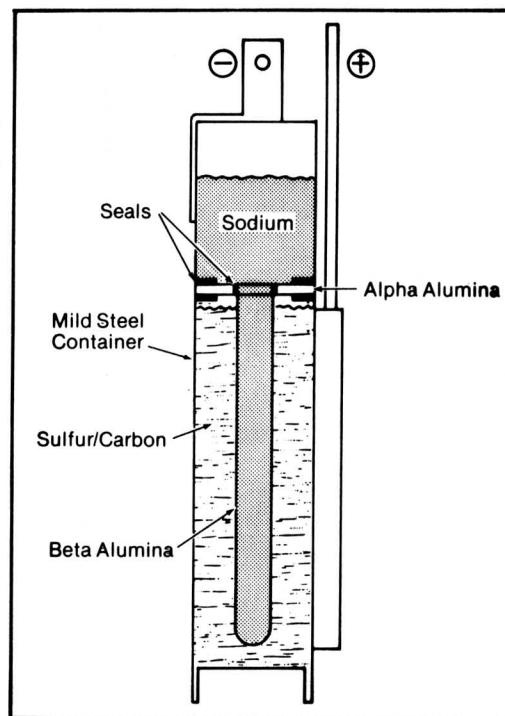


Figure 1. Laboratory sodium-sulfur cell configuration.

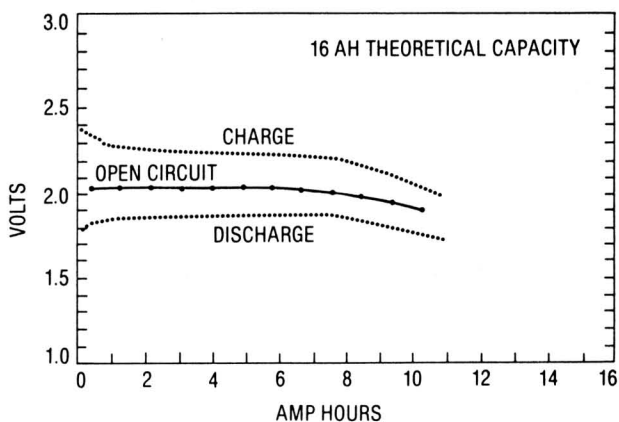


Figure 2. Charge-discharge behavior of a sodium-sulfur cell.

## 2.2 Applications

### 2.2.1 Electric Utilities

Figure 3a shows a typical weekly load curve for an electric utility. In the absence of electric energy storage — and there are very few ways in which electric energy can be stored — energy must be stored in some other form or generated on demand. The most efficient power generation methods, such as nuclear or large fossil-fueled steam turbines, are not amenable to *load-following*, and are used for *base-load* power. The less efficient methods, such as combustion turbines, are used during peak demand periods, for load-following, and to provide *spinning reserve*. If the Beta Battery were used for peak power and load-following, overall utility system efficiency would increase and fuel substitution would be accomplished by increasing the relatively fuel-efficient base-load duty and replacing the

fuel-inefficient peaking turbine with the Beta Battery, as shown in Figure 3b. The battery would be charged by the base load device during low demand periods and discharged during peak demand periods. In addition, the rapid discharge response of a battery permits use as a ready or "spinning" reserve, without constant wasted fuel consumption as with other devices.

In a typical utility installation, a storage capacity of 100 MWh would be installed for a planned five hour discharge at a 20 MW rating. This would require somewhat more than one hundred thousand 600 AH cells, a size which has already been built and tested. In order to be economical, a charge-discharge efficiency of 75% and a ten-year, or 2500 cycle, life is required; cost should be less than \$100/kWh. Clearly, the trade-offs between efficiency, life and cost are multitudinous. The

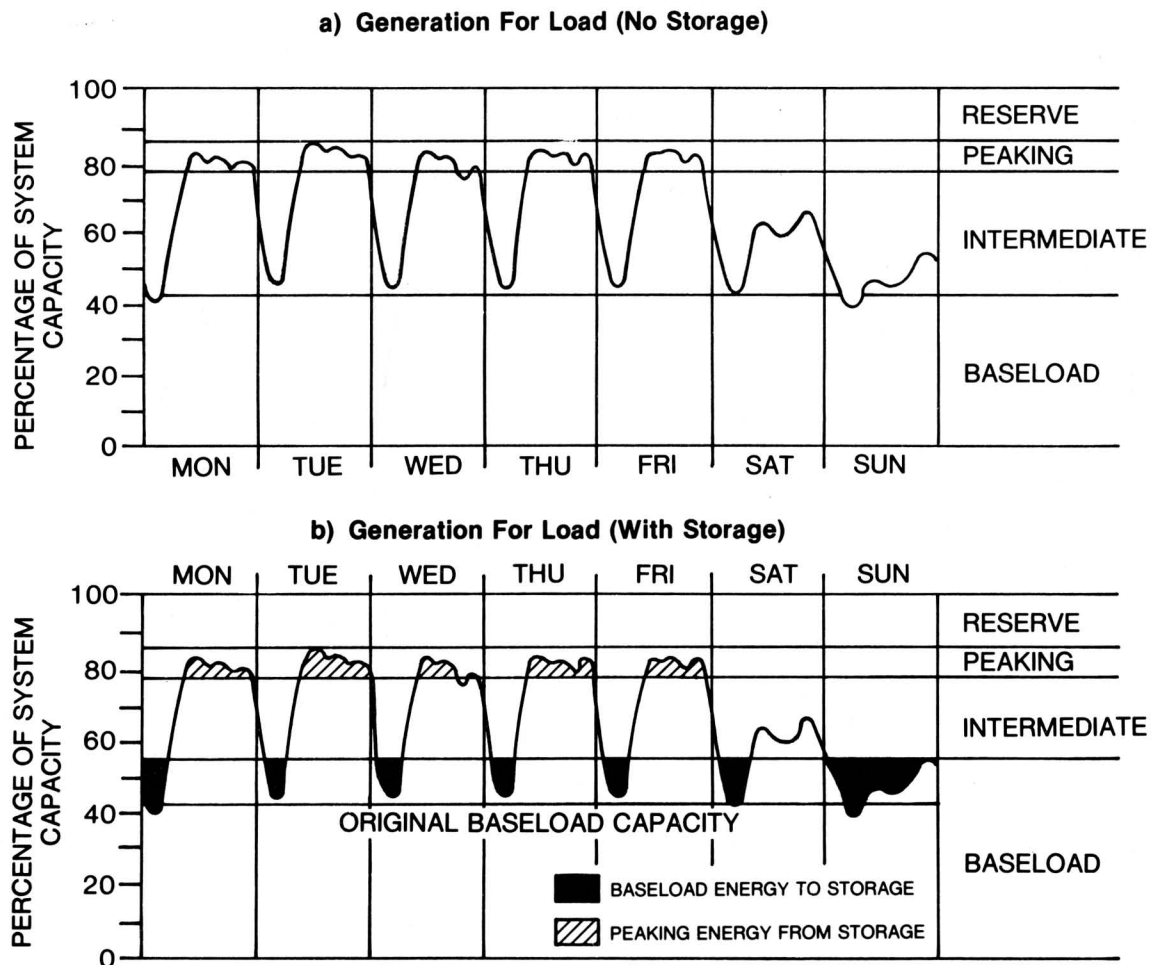


Figure 3. Typical variation in utility load demand.

Beta Battery, however, appears capable of meeting the requirements, and looks more attractive than other advanced battery systems.

### 2.2.2 Electric Vehicles

The electric vehicle offers a somewhat different set of challenges and opportunities for which the Beta Battery is also a candidate. In a sense, the electric vehicle is a form of utility load-leveling, albeit a slightly less controlled one, since vehicle owners would typically charge the cells at night, a period of normally low electricity demand. The vehicle application is less restrictive in terms of life (5 years, 1300 cycles) and cost, but volume and weight — which translate to cell energy and power density — are critical. For adequate acceleration of a small vehicle, 50 kW instantaneous power is needed, while a 50 kWh capacity is needed for a 200 mile range. Beta Batteries with an energy density of 100 Wh/kg can meet these requirements. In contrast, conventional lead-acid cells deliver about 30 Wh/kg.

### 2.3 Technical Progress

Excellent progress has been made in understanding and eliminating technical limitations associated with most of the cell components. For example:

- A patented pack-diffusion process has been developed to protect the low-cost mild steel sulfur container from corrosion. The process results in a duplex, chromium-rich conductive scale. The mechanism and kinetics of coating degradation are well established, and a minimum five-year life for the coating can be expected at the normal temperature of operation. Cost of the coating is moderate.
- The sodium electrode functions reversibly and well indefinitely, with excellent polarization behavior. The purity requirements for sodium have not been clearly established, but even "reactor-grade" sodium which is used in laboratory cells is inexpensive and widely available. The safety of liquid sodium is a key concern, and proprietary approaches for absolute safety are being developed. Crush-tests and overvoltage tests of full size cells have shown that the cell container is not breached even under the most severe conditions.
- The sulfur electrode has been designed for high charge/discharge rates ( $>100\text{mA/cm}^2$ ) by molding randomly distributed graphite fiber

layers with the sulfur such that a higher-resistance fiber layer is located at the electrode/electrolyte interface. During high-rate charging, this design moves the sulfide oxidation reaction away from the interface, thus reducing resistance and concentration polarization, which would result from elemental sulfur deposition on the electrolyte surface. The electrode is capable of operating at twice the design rating for electric utility cells. Capacity retention for this electrode design is constant at about 80% of theoretical. High-purity sulfur is not required. Engineering of the sulfur electrode depends on the cell size and desired charge/discharge.

- The exterior, thermocompression bond has proven durability. The bond, made by heating the steel container halves and an  $\alpha\text{-Al}_2\text{O}_3$  insulator and applying pressure for a short time, has been on test for about three years. More than 2000 seals have been made without a single sudden fracture. Seals are usually helium-leak tight when new, and slow leaks are uncommon.
- The interior, glass seal is still undergoing development, with long-term glasselectrolyte interaction remaining a concern. The key challenge is to find a glass composition which can withstand chemical attack and has the desired thermal expansion match with the adjoining components. By definition, the electrolyte has high sodium-ion mobility and glasses typically contain sodium, so reaction between the glass and the electrolyte — possibly leading to glass devitrification — must be prevented. Through extensive accelerated testing, a borosilicate glass composition has recently been developed to replace an earlier aluminoborate glass. Cell life is not limited by the glass seal, however.
- The solid electrolyte is the key cell component, and also the one which currently limits cell reliability. While some cells have been cycled as many as 3000 times, a 500 cycle life is more typical. Recent results suggest that a major increase in cycle life is likely with a newly formulated electrolyte composition now on test. A discussion of this technically fascinating solid electrolyte material — beta- and beta"-alumina — is given in a following section.
- Cell engineering, manufacturing, and scale-up have kept pace with technology progress, and provided that required improvements are made



in the electrolyte, a significant demonstration of the technology in both utility and vehicle modes is likely by the mid-1980s. Low cost manufacturing of the cell and battery module remains a major challenge, with much of the present engineering development aimed at meeting the cost goals, but the prognosis for success is excellent.

#### 2.4 Development of Beta- and Beta''-Alumina Solid Electrolytes

The ion-conducting separator in the Beta Battery belongs to the family of materials referred to by such names as fast-ion conductor, superionic conductor, or solid electrolyte. These are solid materials which, by virtue of some solid-state ionic defect, conduct ions, often reaching conductivities typical of aqueous electrolytes or molten salts, although generally those conductivity levels are reached only at elevated temperature. Materials are classified by defect type, structure type, and ionic species, but only the beta-alumina family of materials is important here: the solid-state structure of beta-alumina is comprised of discrete spinel structure "blocks" — corresponding to the formula  $\text{Al}_{11}\text{O}_{16}^{+}$  — separated by layers or planes containing sodium and oxygen. Because there are more sodium sites available than are occupied, and because the planes are "held open" by interaction with the spinel block and by bridging oxygen atoms, movement of sodium is facilitated through these "conducting planes," leading to two-dimensional sodium-ion conduction. The particular structure and elements are not prone to electronic defects under conditions of interest. When two spinel blocks separate a conducting plane, the resulting structure is referred to as beta-alumina, whereas three spinel block separation is called beta''-alumina. In actual fact, the differences between beta and beta'' are greater, in that there are differences in the conduction plane, and beta'' appears to require the use of "stabilizers" such as Mg or Li, which replace some of the Al atoms in the spinel block. The phase stability region for both beta and beta'' has been the subject of several investigations, but a complete phase study for the  $\text{Na}_2\text{O}-\text{Li}_2\text{O}-\text{MgO}-\text{Al}_2\text{O}_3$  system would be an exceedingly difficult task.

In terms of practical importance, most of the compositions under active worldwide development are actually solid solutions of both beta and beta'' phases. The beta'' phase has better ionic conductivity ( $1 \text{ ohm}^{-1}\text{cm}^{-1}$  at  $330^\circ\text{C}$  vs.  $0.3 \text{ ohm}^{-1}\text{cm}^{-1}$  for beta single crystals) and is therefore favored,

but beta'' is more difficult to manufacture and more sensitive to various types of degradation. For that reason, prior to 1980, the General Electric program was focused on compositions rich in beta-alumina; recently, a major decision to change the composition to mostly beta'' was made in order to improve conductivity and, therefore, to meet cost goals. The particular formulations under development are proprietary, but composition ranges of interest are 7%-10%  $\text{Na}_2\text{O}$ , 1-5% ( $\text{Li}_2\text{O} + \text{MgO}$ ), balance  $\text{Al}_2\text{O}_3$ .

Equal to the composition in importance is the technique by which useful polycrystalline, sintered shapes are fabricated. General Electric uses electrophoretic deposition to form the green shape — a tube, 1 mm thick, 10 mm in diameter and 15 cm in length for laboratory scale cells. The electrophoretic process involves preparation of a suspension of controlled particle size ( $\sim 3 \mu\text{m}$ ) precursor powder in amyl alcohol. The suspension is charged by milling for several hours, and then poured into a metal container with a stainless steel mandrel in the center. When a dc potential is applied between mandrel and container, the negatively charged particles deposit on the positively charged mandrel. Only a few minutes at 500 V is required. Figure 4 pictorially shows the process. The material is then dried, removed from the mandrel and sintered in a continuous zone-furnace at temperatures between  $1600-1700^\circ\text{C}$ . Sintering of the greenware is carried out in  $\alpha\text{-Al}_2\text{O}_3$  tube enclosures to prevent preferential loss of the more volatile  $\text{Na}_2\text{O}$ . The sintering brings the density from about 55% (as deposited) to better than 99% of theoretical. This sequence results in a high-quality ceramic with a uniform, fine-grain microstructure ( $3 \mu\text{m}$  grains), and good strength (45 kpsi). Microstructure is particularly important because of the two-dimensional nature of ionic conduction; large grains tend to focus current in particular regions, causing electrical stresses during use. The resistivity of tubes of most recent vintage is  $6 \text{ ohm-cm}$  at  $330^\circ\text{C}$ .

Initial in-cell performance of beta''-alumina tubes is excellent. Early problems with a higher apparent beta''-alumina tube resistance in the discharge mode than in the charge mode have been eliminated through minor modifications in the composition. The critical remaining unknown with this new composition is long-term degradation of the material. This degradation may be manifested through a variety of observations, including general darkening and localized blackening of the initially white tube, corrosion-like scaling on the sulfur-exposed surface, slow increase in resistance with time, and fracture of the tube. These conditions are

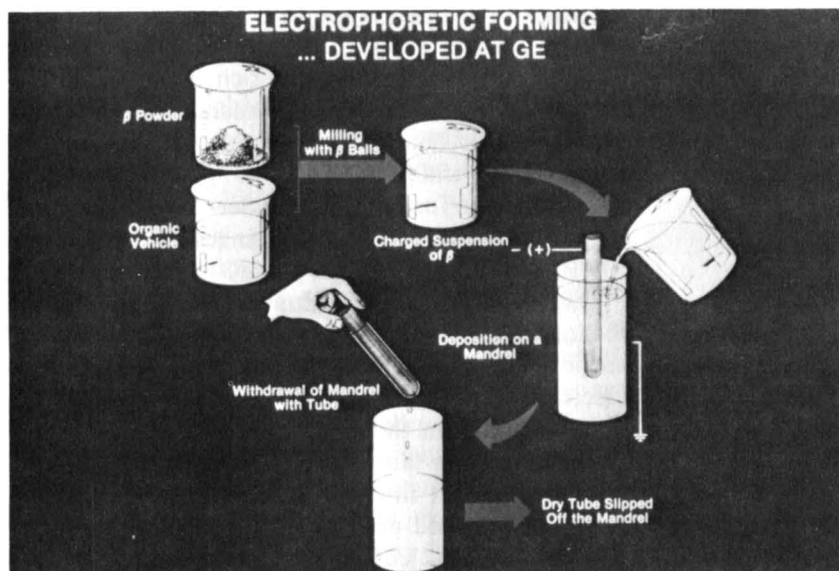


Figure 4

Electrophoretic forming of beta-alumina tubes.

much less frequently seen with the new composition; nevertheless, evidence is quite strong that, except for early failures due to poor assembly or component defect, failure of the ceramic limits cell life; this is not to say that some cell component other than the ceramic does not affect the ceramic in such a way that the end result is ceramic failure. The typical, or mean time to failure for cells tested in 1980 was on the order of 500 charge-discharge cycles. However, some cells have operated well for as many as 3000 cycles, giving firm evidence that failure is not fundamental in nature. It is anticipated that tripling of average cycle life will be accomplished in the 1981-1982 time-frame. It is also useful to point out that certain failure observations reported by other researchers, such as the onset of electronic conduction, have not been seen in General Electric cells.

The study of solid electrolyte failure modes is presently the subject of intense effort at General Electric. The diversity of degradation observations, their sporadic nature, and their interrelationship make for a difficult technical challenge. Impurity effects and voltage/current breakdown are two theories which have demonstrated validity, although many other theories are being evaluated. In the case of impurity effects, it is well-established that certain cation species, such as calcium and potassium, can replace sodium ions in the conducting plane of the ceramic. Not only does this increase the bulk resistivity of the ceramic, but it causes more current to be carried by the lower-resistance sodium-ion conducting regions. This may relate to the observation that breakdown of the material can

occur at potentials of greater than  $\sim 4$  V and current breakdown may occur at current densities in excess of  $500 \text{ mA/cm}^2$ . Measures are being taken to avoid these and other known sources of degradation, but clearly other degradation modes are also operating.

## 2.5 Summary

The Beta Battery has excellent near-term prospects for both electric utility and electric vehicle applications. In both applications, an increase in energy efficiency and a shift from premium fuels to available fuels can be realized. The General Electric program has made excellent technical progress, and a major demonstration by the mid-1980s is possible. The key technical development need is for improved cell reliability; currently, cell reliability is believed to be limited by the solid electrolyte separator.

## 3. THE CARBONATE FUEL CELL FOR POWER GENERATION

Fuel cells are essentially storage batteries in which the reactants are continuously replenished and the products are continuously removed. This extra degree of freedom — reactant flow — gives the ability to provide continuous and variable power output, but the definition and measurements of "performance" and efficiency become more complicated. In addition, fuel cells cannot themselves store energy, although energy can be stored as fuel and oxidant, analogous to rotating machinery. Like the battery, fuel cells are highly efficient, but overall system efficiency must take into considera-



tion the efficiency losses associated with preparing the fuel and disposing of fuel which is not consumed in the cell.

The simplest type of fuel cell is a hydrogen-oxygen cell which uses either an acid or alkaline electrolyte. These cells have been used successfully for many years in military and aerospace applications. Because the cells operate at modest temperatures, typically less than 200 °C to prevent boiling of the electrolyte, noble metal catalysts — such as platinum — are required to facilitate the electrode reactions; the catalysts, in turn, are poisoned by certain contaminants, such as carbon monoxide in the fuel, yielding the further requirement of reasonably pure hydrogen fuel. Alkaline electrolyte cells cannot utilize carbonaceous fuels at all because of reaction with alkaline electrolytes to form carbonates. These factors conspire to make low-temperature systems a difficult challenge with respect to cost and overall efficiency, but excellent progress has been made, as evidenced by 4.8 MW demonstration phosphoric acid fuel cell power plants now under construction in New York City and Tokyo.

At the opposite extreme, very high temperature (1000 °C) fuel cells using zirconia-based oxygen-ion conducting solid electrolytes have been explored. These cells have the advantages of excellent fuel-composition tolerance and no need for catalysts, but the very high temperatures needed for adequate oxygen ion conductivity complicate sealing, current collection, and heat-exchange requirements.

Intermediate temperature fuel cells using molten salts appear to offer an excellent compromise between the two extremes. Operating at 650 °C, the molten carbonate fuel cell does not require noble metal catalysts, cell reactions are fast, and virtually any gaseous fuel containing H<sub>2</sub> and CO can be used; in addition, the availability of waste heat at 650 °C is convenient for use in either cogeneration schemes or auxiliary power generation cycles.

### 3.1 The Carbonate Cell

The molten carbonate fuel cell generates electricity by the electrochemical reaction of fuel at the cell anode and oxidant at the cell cathode. Figure 5 shows the concept schematically. Hydrogen is consumed electrochemically at the anode via the reaction:



while carbon monoxide is used indirectly to reduce

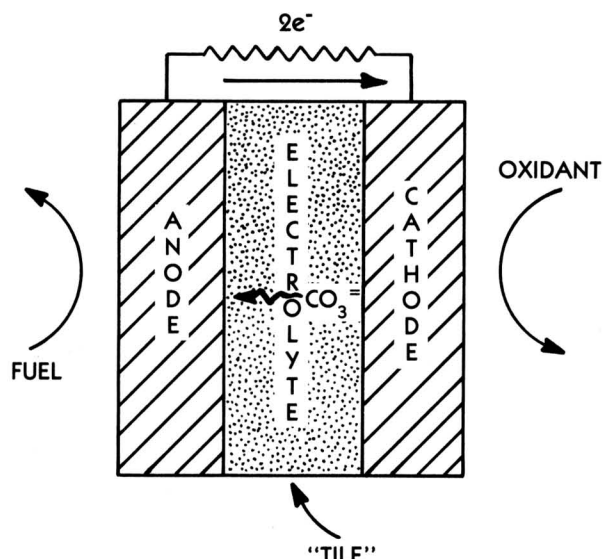
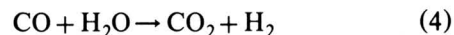
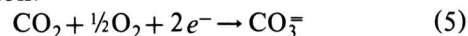


Figure 5. Carbonate fuel cell concept.

water and produce more hydrogen via the water gas shift reaction:



Recycled carbon dioxide from the spent fuel is added to oxygen from fresh air to supply the cathode for the reaction:



The cycle is completed by the transfer of carbonate ions through the electrolyte and electrons through the external circuit.

Although carbonate cells have been actively under development for about 25 years, the present configurations and materials have been developed within the last five to ten years. State-of-the-art cells use porous nickel-based anodes and porous lithiated nickel oxide cathodes. The electrolyte structure, commonly referred to as the "electrolyte tile" because of its configuration and appearance at room temperature, is a composite material comprised of a Li<sub>2</sub>CO<sub>3</sub>/K<sub>2</sub>CO<sub>3</sub> electrolyte mixture and an inert, nonconducting LiAlO<sub>2</sub> powder matrix. Cell housings and current collectors, exposed to both reducing and oxidizing environments in the presence of molten carbonate, are usually made of oxidation and corrosion-resistant alloys such as AISI 316 stainless steel.

Cells are generally operated using dilute fuels to simulate low-Btu coal gasification products, and dilute oxidants to simulate air-feed. Single-pass fuel utilization is typically 70-75% (based on total H<sub>2</sub> + CO used vs. total H<sub>2</sub> + CO available). Selected

cells have been operated with  $\text{H}_2\text{S}$  and  $\text{HCl}$  contaminants to more closely simulate real fuels. Laboratory cells have an active area of  $100\text{ cm}^2$ , and operate at  $160\text{ mA/cm}^2$  and a cell potential of  $\geq 0.7\text{ V}$  (for a fuel/oxidant combination having an open circuit potential of  $1.040\text{ V}$ ) at  $1\text{ atm}$  pressure.

Figure 6 shows typical performance curves for fixed fuel and oxidant utilizations. Laboratory cells have a planar configuration, with a  $0.030\text{ inch}$ -thick anode, a  $0.015\text{ inch}$ -thick cathode, and a  $0.070\text{ inch}$ -thick electrolyte structure. Figure 7 shows the simplest laboratory configuration.

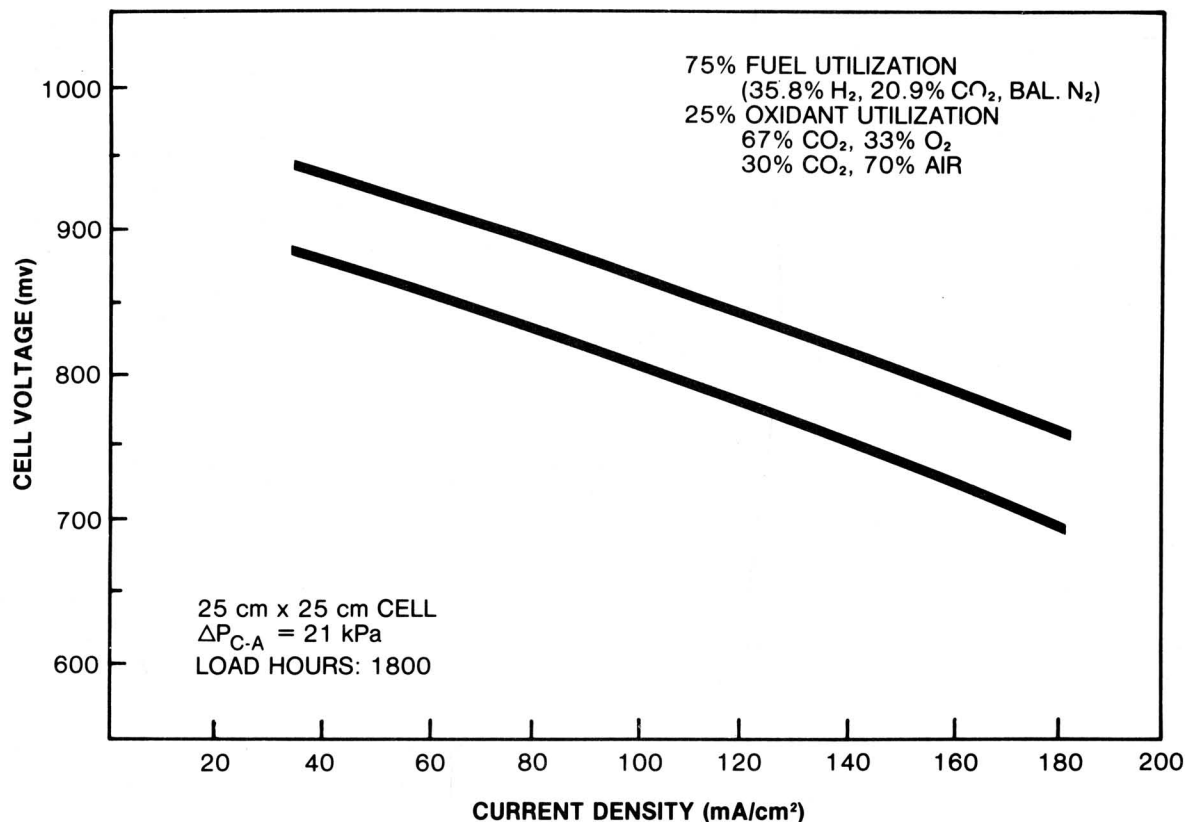


Figure 6. Performance of a carbonate fuel cell: upper curve, rich oxidant; lower curve, dilute oxidant.

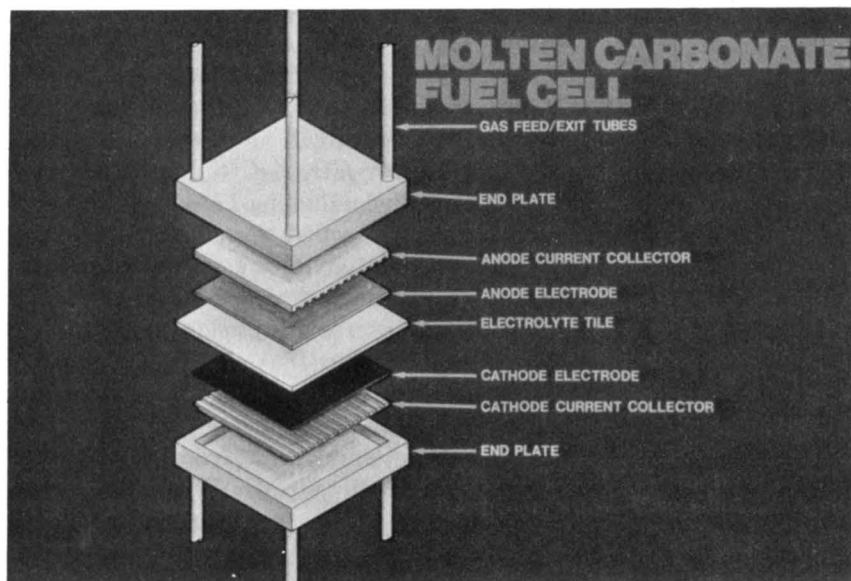


Figure 7

Laboratory carbonate fuel cell configuration.

### 3.2 Applications

Fuel cell systems are generally recognized to have the virtues of high power generation efficiency (even at part load), environmental compatibility, and modular flexibility. In addition, the molten carbonate cell is uniquely suited to fossil-fueled systems because of its straightforward utilization of carbon monoxide as a fuel. Several studies have shown that coal-fired carbonate fuel cell power plants can produce electricity from coal at better than 45% efficiency, with a cost-of-electricity comparable to other advanced power generation concepts. The high efficiency of molten carbonate systems is in part made possible by the high temperature operation of the fuel cell, which yields high-grade rejected heat for use in a bottoming cycle.

Figure 8 shows a typical coal-fired, central-station, power-plant design incorporating a coal gasifier, gas clean-up system, fuel cell, and steam and gas turbines. A plant size of approximately 675 MW ac was selected as typical of present base-

load fossil fuel plants. The plant is modularized, consisting of five identical power modules and a steam turbine generating plant. Each of the five power modules are also modular, containing 18 fuel cell modules, 3 gasifiers, 2 heat recovery steam generators, 2 compressors, 1 gas turbine-generator set and 1 fuel gas cleanup train. The overall plant efficiency of this system is estimated to be about 50 percent. The fuel cell module would have an expected life of 6 years and a cost of \$60/kW.

Other systems have also been considered; for example, an oil-fired dispersed site plant, with no bottoming cycle and low capital cost, might have an efficiency on the order of 45%. Natural-gas fired systems, with cogeneration energy credit, might have efficiencies approaching 90%. Most emphasis, however, is being placed on the large base-load coal-fired systems.

While low-temperature fuel cells are being considered for smaller applications, such as home or apartment power, or electric vehicles, the carbonate fuel cell is not a good fit to these applications because of its high operating temperature.

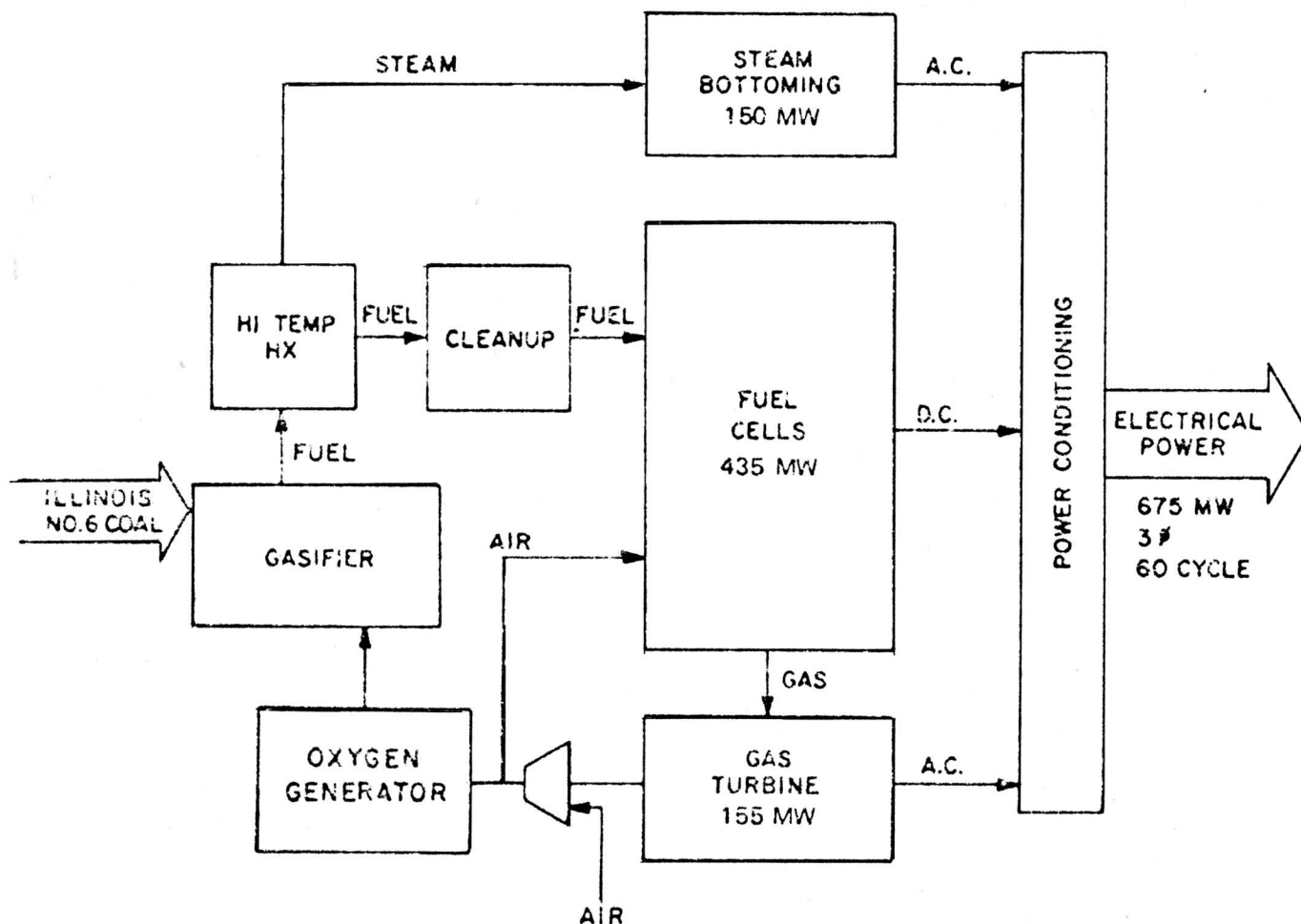


Figure 8. Design of a coal-fired carbonate fuel cell power generation cycle.



### 3.3 Technical Progress

The initial carbonate fuel cell performance is already at a level consistent with requirements for a commercial system. Most development effort is now directed toward improved cell component materials and fabrication processes and toward understanding of fundamental cell functional mechanisms, in an effort to extend the economic life of cells to at least 40,000 hours. While some cells have been successfully operated for thousands of hours, performance generally exhibits a slow decay which results from a combination of phenomena such as hardware and current collector corrosion, electrolyte loss, and changes in the physical characteristics of the porous electrodes and electrolyte structure. Sudden failure, while not common, can result from cracking of the electrolyte structure, a phenomenon which is promoted by thermal cycling of the cell to below the 490 °C freezing point of the electrolyte. Since the cost of cell materials and their fabrication into components are significant issues, the materials development activities are guided by the need to simultaneously improve the material properties while reducing the finished cell component cost.

### 3.4 Electrolyte Development

The present generation of electrolyte structures consists of a mixture containing 50-60 wt.% (55-70 volume %) of the near-eutectic electrolyte composition: 62 mole %  $\text{Li}_2\text{CO}_3$  + 38 mole %  $\text{K}_2\text{CO}_3$  matrixed in a bed of small crystallite size ( $\sim 0.5 \mu\text{m}$ )  $\text{LiAlO}_2$  powder. The packing of the matrix phase particles is critical because retention of liquid electrolyte in the matrix interstices is governed by the size of the interstices. The conventional method of electrolyte structure preparation involves the synthesis of an intimate mixture of matrix and electrolyte powder, followed by hot-pressing just below the electrolyte liquidus (490 °C) and at pressures as great as 50 MPa. Because of the requirement for agglomerate-free, high-surface area matrix powder, synthesis of what would appear to be a simple material is indeed quite challenging. There are three different crystallographic modifications of  $\text{LiAlO}_2$ , with differing densities, so structure control during synthesis is also important.

To exemplify the importance of particle size control, compare the capillarity pressure of a  $0.5 \mu\text{m}$  pore containing molten carbonate (15,800 psi) with a  $2 \mu\text{m}$  pore (4 psi). Thus, if all pores were  $0.5 \mu\text{m}$ , the structure should be capable of withstanding 15,800 psi of differential pressure.

Particle size control is also important because the electrode pores must be larger by about a factor of ten, such that controlled release of electrolyte to the electrode occurs. If too much electrolyte is released, the electrode pores "flood," while the electrode is dry if not enough electrolyte is released; both extremes lead to poor electrode performance. The characteristics of the matrix powder, then, are probably the single most important — and most delicate — factor controlling proper cell functioning.

The General Electric Program has devoted significant attention to the electrolyte structure problem, and several advanced synthetic and fabrication processes for electrolyte structure preparation have been developed. One modified synthetic process is the preparation of electrolyte-free matrix  $\text{LiAlO}_2$  by the reaction of Li and Al species (oxides, hydroxides or carbonates) in the presence of molten alkali chloride mixtures, which function solely as solvents for reaction. The product  $\text{LiAlO}_2$  crystallites are retrieved from the chloride solvent by aqueous processing. Due to unavoidable agglomeration of the  $\text{LiAlO}_2$  during synthesis, the material must be de-agglomerated by mild comminution. Since the alkali chloride reaction medium is separated from the product, it is possible to include additional product-modifying species so long as they can be removed with the chlorides. Particle sizes on the order of  $0.3 \mu\text{m}$  are obtained.

The electrolyte-free matrix material can be converted into a mixture suitable for hot-pressing by simple blending of the  $\text{LiAlO}_2$  with the solid carbonates followed by melting of the carbonates. This mixture, lightly comminuted to facilitate subsequent processing, behaves similar to a conventionally prepared mixture.

The electrolyte-free matrix material also provides an opportunity to separate the commercially unattractive hot-pressing process into two more advantageous steps. In one process, the electrolyte-free  $\text{LiAlO}_2$  is pressed to 30-45% of theoretical density by room-temperature die pressing. The pressed material can be impregnated with carbonate by heating a layer of carbonate powder placed on the pressed matrix. If the impregnation is carried out slowly and on a porous substrate to allow gas to escape from the matrix pores, complete filling of the structure can be accomplished without disruption. A second process, similar to the one used to fabricate beta-alumina tubes, is the use of electrophoretic deposition to deposit a layer of  $\text{LiAlO}_2$ . Deposition of a 0.070 inch-thick layer can

be accomplished in 30 seconds using a 500 V potential and a suspension of  $\text{LiAlO}_2$  in isopropanol. The electrophoretically deposited matrix can then be impregnated as just described.

Synthesis and fabrication are not the only challenges posed by the present electrolyte structure, however. Slow loss of electrolyte with time, cracking on thermal cycling, and changes in  $\text{LiAlO}_2$  morphology with time are additional problems.  $\text{LiAlO}_2$  appears to undergo morphology changes by two mechanisms: slow grain growth (i.e., sintering) and structural rearrangement. Both mechanisms can result in an electrolyte structure which has altered porosity and, consequently, different electrolyte retention characteristics. While relatively little progress has been made in solving these problems directly, significant activity has been directed toward exploring alternate materials as an approach to avoiding the problems. As improvements to the  $\text{LiAlO}_2$ -based structures continue to be pursued,  $\text{SrTiO}_3$  has been proposed as a possible superior replacement.

A synthesis procedure, analogous to the "chloride" synthesis for  $\text{LiAlO}_2$ , has been developed to prepare  $\text{SrTiO}_3$  from  $\text{SrCO}_3$  and  $\text{TiO}_2$ . Indeed, because  $\text{SrTiO}_3$  is less sensitive to water than  $\text{LiAlO}_2$ , the synthesis procedure is even simpler, and readily yields "tile quality" powder. Because  $\text{SrTiO}_3$  has only one crystallographic modification, the cubic perovskite structure, opportunities for morphology changes are diminished. The material is highly stable toward carbonate, and electrolyte structures have been prepared by both hot-pressing and impregnation techniques. Early in-cell testing indicates equivalent initial cell performance, but  $\text{SrTiO}_3$  appears to have a much slower particle-growth rate.

### 3.5 Electrode Development

The present electrode system has functioned quite adequately in short-term tests. Early in the program, pure nickel anodes were used, and sintering of the nickel caused rapid performance degradation after about 500 hours. An out-of-cell anode sintering study, undertaken to understand and quantify morphological changes, showed that electrodes which were originally 66% porous decreased to only 37% porosity after 1600 hours. Nickel anodes have been replaced by Ni/Cr anodes, which have far better sintering resistance, and electrode development has shifted toward the goal of reduced cost via replacement of nickel. A process has been developed in which inert  $\text{SrTiO}_3$  particles are electroless-plated with thin layers of nickel, such that only a small fraction of the amount of nickel is

required to give the same electrochemical surface area and pore characteristics. Both types of anodes have been made in dual-porosity configurations, with smaller pores near the electrolyte interface and larger pores near the current collector interface. The higher surface area of the small pores improves reactivity, and the coarse pores promote gas phase transport. Results show that dual porosity electrodes (3  $\mu\text{m}$  small pores and 10  $\mu\text{m}$  large pores) perform as well as standard electrodes at low current density, but much better than single porosity at high current density.

Cathode development is focused on two problems: improved control of porosity and strength, and better performance. Standard cathodes are formed by oxidation and lithiation of a porous nickel plaque during cell start-up; consequently, control of the pore structure is not possible, and the resulting cathode is weak and brittle. An out-of-cell technique for lithiated nickel oxide cathode fabrication has been developed at General Electric: A factor of three increase in cathode strength was achieved by reactive sintering of pressed lithium salt/nickel/binder powder composites. Polarization losses at the cathode are about twice those at the anode. This appears to result in part, at least, from the relatively high resistivity of lithiated nickel oxide, 10 ohm-cm at 650 °C. Thus, there is an active search for an electronically conducting material which is stable toward oxygen in the presence of molten carbonate. Relatively few materials meet the criteria, but lithiated  $\text{CuO}$  and complex oxides of Li and Fe are being considered.

### 3.6 Hardware Materials

AISI 316 stainless steel has been used as the material of construction for the cell housing, anode and cathode current collectors, and gas inlet and exit ducts. An aluminum coating, which oxidizes to form an electrically insulating layer, protects the stainless steel housing in the seal area, where the housing contacts the electrolyte structure. Since good conductivity is a requirement for the current collector, aluminizing cannot be used for corrosion protection.

The anode current collector is the site most susceptible to corrosion, with occasional catastrophic corrosion leading to premature cell failure. The catastrophic corrosion is manifested by excessive consumption of material, with the corrosion severity increasing from the gas inlet region to the gas outlet region (i.e., more oxidizing environment). Corrosion is also more severe at the points of electrode contact suggesting that liquid electrolyte is in-

volved in the mechanism. Carburization is also observed, (measured carbon contents are a factor of ten higher than in the starting material), with intergranular corrosion promoted by carbide precipitation. A preliminary mechanistic study showed that dissolution of iron, possibly as  $\text{LiFe}_5\text{O}_8$ , in the electrolyte under mildly oxidizing conditions, followed by reprecipitation under open circuit or low current conditions — a typical hot corrosion mechanism — was responsible. Quite interestingly, the cathode current collector does not show excessive corrosion; the apparent protection mechanism is the insolubility of a Fe/Ni outer layer in the electrolyte.

The mechanistic work has led to improved materials. In particular, AISI 310 stainless steel, with higher chromium content, has shown improved corrosion resistance at both anode and cathode, and chromium coatings on the anode side offer additional protection. Out-of-cell tests, based on thermogravimetric analysis, indicate a factor of ten improvement in the rate of corrosion scale formation under anode gas conditions for chromium-coated 310 stainless steel. Protection arises from the insolubility of chromium in the electrolyte under anode conditions. In-cell validation is in progress.

### 3.7 Summary

Molten carbonate fuel cells are extremely attractive for incorporation into advanced, highly efficient utility power generation systems based on coal. High single cell performance under increasingly realistic and demanding conditions continues to support the realization of an efficient fuel cell power plant. Effort is now directed toward meeting the challenges of improved cell life and more cost-effective cell materials and fabrication methods. Although the overall status of development is several years behind the sodium-sulfur battery, both systems show promise as commercial electrochemical technologies to conserve our energy resources.

### ACKNOWLEDGEMENT

Many man-years of effort by scientists and engineers at General Electric are reflected in this effort. Although their names are too numerous to mention, their work has made this paper possible, and their contributions are gratefully acknowledged.

### REFERENCES

1. N Weber and JJ Kummer, Proc. 21st Power Sources Conference, P. 37.



H81CRD258  
CAMPBELL VC 6065102090  
GENERAL ELECTRIC CO.  
TB DEPT 6-183 EP  
SYRACUSE NY 13221

Browall, KW ELECTROCHEMICAL ENERGY STORAGE  
AND CONVERSION

Report No. 81CRD258  
November 1981

---

GENERAL ELECTRIC COMPANY  
CORPORATE RESEARCH AND DEVELOPMENT  
P.O. BOX 8, SCHENECTADY, N.Y. 12301

---

GENERAL  ELECTRIC