Carbonate fuel cells: Milliwatts to megawatts

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Abstract

The carbonate fuel cell power plant is an emerging high efficiency, ultra-clean power generator utilizing a variety of gaseous, liquid, and solid carbonaceous fuels for commercial and industrial applications. The primary mover of this generator is a carbonate fuel cell. The fuel cell uses alkali metal carbonate mixtures as electrolyte and operates at ∼650 °C. Corrosion of the cell hardware and stability of the ceramic components have been important design considerations in the early stages of development. The material and electrolyte choices are founded on extensive fundamental research carried out around the world in the 60s and early 70s. The cell components were developed in the late 1970s and early 1980s. The present day carbonate fuel cell construction employs commonly available stainless steels. The electrodes are based on nickel and well-established manufacturing processes. Manufacturing process development, scale-up, stack tests, and pilot system tests dominated throughout the 1990s. Commercial product development efforts began in late 1990s leading to prototype field tests beginning in the current decade leading to commercial customer applications. Cost reduction has been an integral part of the product effort. Cost-competitive product designs have evolved as a result. Approximately half a dozen teams around the world are pursuing carbonate fuel cell product development. The power plant development efforts to date have mainly focused on several hundred kW (submegawatt) to megawatt-class plants. Almost 40 submegawatt units have been operating at customer sites in the US, Europe, and Asia. Several of these units are operating on renewable bio-fuels. A 1 MW unit is operating on the digester gas from a municipal wastewater treatment plant in Seattle, Washington (US). Presently, there are a total of approximately 10 MW capacity carbonate fuel cell power plants installed around the world. Carbonate fuel cell products are also being developed to operate on coal-derived gases, diesel, and other logistic fuels. Innovative carbonate fuel cell/turbine hybrid power plant designs promising record energy conversion efficiencies approaching 75% have also emerged. This paper will review the historical development of this unique technology from milliwatt-scale laboratory cells to present megawatt-scale commercial power plants.
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1. Basic concept

The basic electrochemistry of carbonate fuel cells involves formation of carbonate ($CO_3^=$) at the cathode by the combination of oxygen, carbon dioxide and two electrons; transport of the carbonate ions to the anode through the carbonate electrolyte; and finally, reaction of the carbonate ion with hydrogen at the anode producing water, carbon dioxide, and two electrons. For each mole of hydrogen consumed in the anode compartment, 1 mol of carbon dioxide and 1 mol of water are produced. Hydrogen is made available to the anode from a fuel (such as by steam reforming natural gas). The CO present in the reformed fuel is also considered a fuel in this fuel cell. The oxygen is supplied from air and the carbon dioxide is made available by recycling the carbon dioxide from the anode exhaust. For this purpose the anode exhaust is oxidized with the feed air in an oxidizer prior to introduction to the cathode. Details of carbonate fuel cell chemistry and system considerations are available in the Fuel Cell Handbook [1].

The fuel cell reactions utilize both H_2 and CO at the anode. The commonly available carbonaceous fuels need to be converted to the fuel cell useable form. Steam reforming of a light hydrocarbon fuel in an external reformer is a well-established industrial process for hydrogen production for fuel cells. The steam reforming reaction is highly endothermic and the fuel cell anode reaction is exothermic. While the product of the reforming reaction (hydrogen) is a reactant in the fuel cell anode, the fuel cell reaction product (water) is a reactant in the reforming reaction. The carbonate fuel cell system operates at high enough temperatures to allow practical reforming reaction kinetics for the natural gas and other light hydrocarbons in the fuel cell. Therefore, the thermal and chemical features of the fuel cell and reforming reactions are uniquely complementary for an efficient integration of both of these reactions inside the anode compart-

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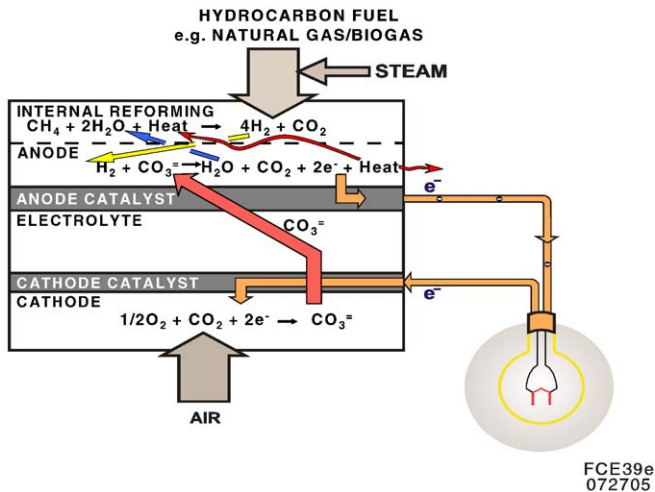 *E-mail address:* mfarooque@fce.com (M. Farooque).

Fig. 1. How the direct carbonate fuel cell works: synergistic and efficient heat and mass transfer results in high dfc efficiency.

ment of the carbonate fuel cell. FuelCell Energy (FCE), Danbury, CT (USA) adopted the internal reforming approach for its high temperature technology and designated its fuel cell as the Direct FuelCell® (DFC®). The DFC operating principle is illustrated in detail in Fig. 1. The overall fuel cell reaction is simply a hydrocarbon fuel conversion with air to electricity, heat, water and CO_2. A hydrocarbon fuel such as natural gas is introduced into the anode compartment along with steam. Unused fuel from the fuel cell is oxidized with fresh air and is introduced to the cathode side. In the presence of the catalyst in the anode compartment, the fuel and water react to form hydrogen fuel. The heat required for the reaction is provided by the fuel cell. The hydrogen reacts electrochemically with $CO_3^=$ at the anode to

release water, CO_2 and heat (which is consumed in the reforming reaction and the remainder is removed from the fuel cell for steady state operation). Two-thirds of the heat produced by the fuel cell reaction is used up in the internal reforming reaction, resulting in uniform fuel cell temperature. This "one-step" process leads to a simpler, more efficient and cost-effective energy conversion system compared with external reforming fuel cells.

2. Carbonate fuel cell technology

A brief development history of carbonate fuel cell technology is shown in Fig. 2. A concise review of early work was presented by Liedhafsky and Cairns [2]. Broers [3] started fuel cell testing in the late 1950s. The basic cell design was defined in the 1960s while the high performance components were identified in the 1970s. The chemical and electrochemical understanding developed during this period is reviewed by Selman and Maru [4]. Fundamental pore equilibrium and capillary control model by Maru and Marianowski [5] provided the invaluable guidance to optimize cell components design. Between 1980 and 2000, component and stack technologies were further improved, simplified and verified in large-area stacks. The internal reforming concept introduced by Baker and Dharia [6] was a breakthrough, leading to efficient and simple system described by Farooque [7]. Manufacturability and proof-of-concept power plants were demonstrated in >200 kW field-testing. Since 2000, the development focused on field trials and commercialization. Over 40 units ranging from 250 kW to 1 MW have been successfully operated, the majority of them by FuelCell Energy.

The carbonate fuel cell operates at an optimal temperature of approximately 600–650 °C that avoids the use of noble
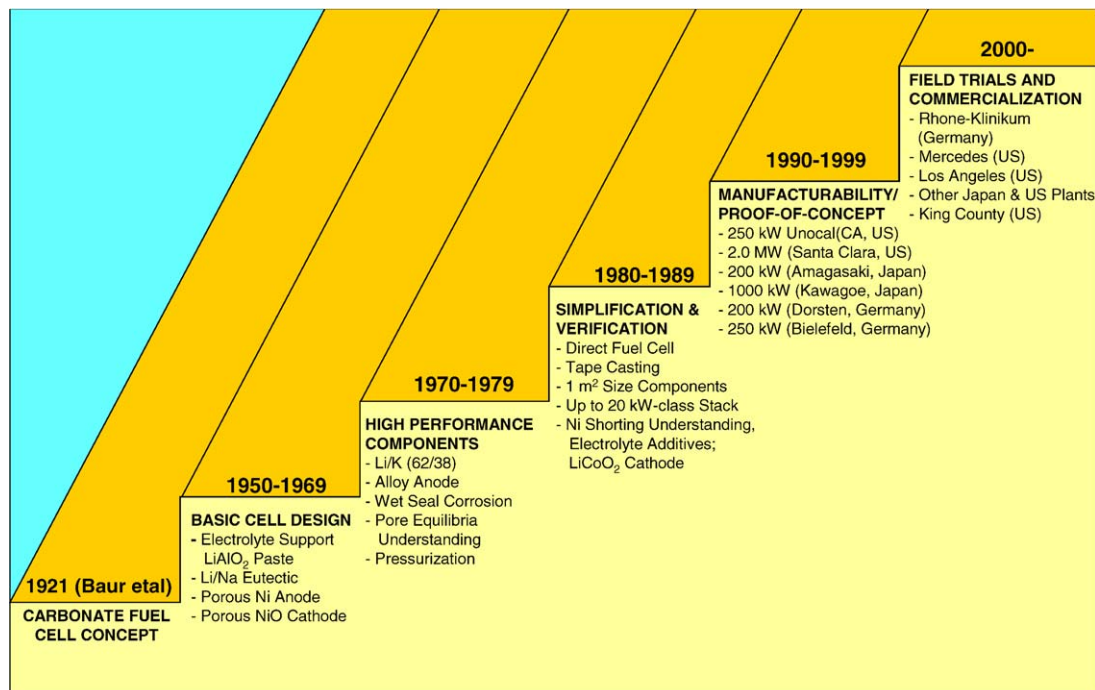

Fig. 2. Development history of carbonate fuel cell: intensive global r&d during the past three decades advanced the technology to commercial level.
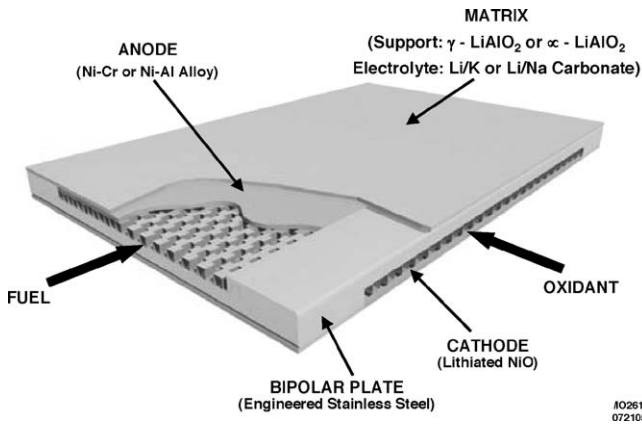
Fig. 3. The carbonate fuel cell bipolar cell package configuration: cell construction employs 300-series stainless steel, and electrodes are nickel-based; all commodity materials.

metal electrodes required by lower temperature fuel cells, such as PEM and phosphoric acid, and the more expensive metals and advanced ceramic materials required by higher temperature solid oxide fuel cells. Less expensive electro-catalysts and readily available commercial metals are used in the carbonate fuel cell design. The Direct FuelCell uses a simple construction as illustrated in Fig. 3. The bipolar plate and the corrugated current collectors are made of 300-series stainless steel. The electrodes are made from porous nickel-based mate-

rials. The fuel and air isolating membrane is a porous ceramic lithium aluminate that holds an electrolyte mixture of lithium and potassium/sodium carbonate salts, which melt between 450 and 510 °C. Material properties such as creep strength, sintering resistance, low compaction, hot corrosion resistance, low carburization, etc. will impact cell life and durability. Stable, long-term anode and cathode electrochemical activity is also required.

The present day carbonate fuel cell materials design is based on intensive materials research carried out during the last three decades, endurance results, and cost considerations. A discussion of various carbonate fuel cell component designs and improvement opportunities is presented below and additional details can be found in the carbonate fuel cell literature reported by Hoffmann et al. [8].

2.1. Anode

Unalloyed porous nickel anodes used by early developers were found to shrink during operation under the stack compressive load, resulting in undesired dimensional change, reduced surface area, and lower electrochemical performance. Alloying with chromium and/or aluminum provides oxide dispersion strengthening resulting in adequate creep strength. Excellent mechanical and chemical stability of the baseline Ni–Al anode is verified in an 18,000 h field operation (Fig. 4 shows similar
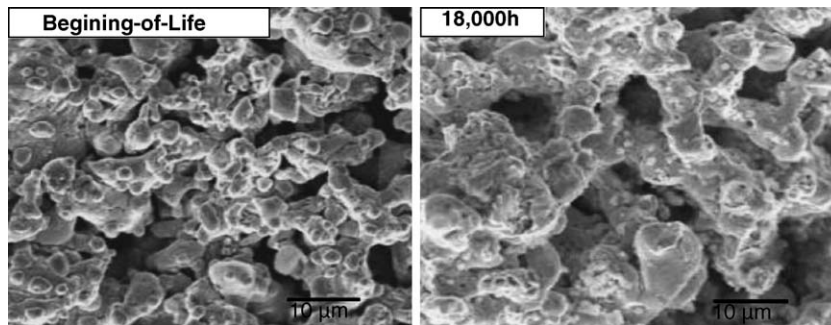

Fig. 4. Anode after 18,000 h service: excellent structural integrity and no change in morphology.
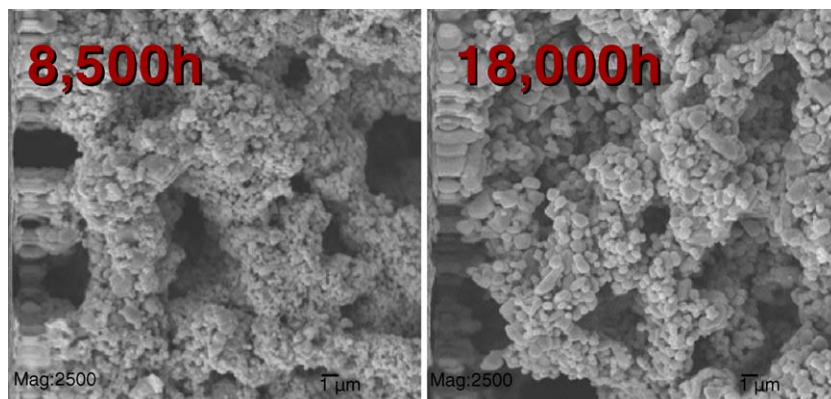

Fig. 5. DFC® cathode in field operation: only very slight particle coarsening occurred during long-term operation.

structure for fresh and used anodes). The anode shows adequate structural integrity and electrochemical activity that can be projected to >5-year life.

2.2. Cathode

The carbonate fuel cell cathode material is lithiated NiO from the beginning of development. This component is known to have a finite solubility in the electrolyte. The extent of its dissolution is controlled mainly by electrolyte composition, applied gas atmosphere, operation pressure and temperature. FCE selected atmospheric pressure system to assure minimal dissolution and adequate long-term life for the cathode. Long-term field operation has shown no issues relating to particle coarsening, indicating a stable structure (Fig. 5).

Opportunities exist in further extending the cathode material stability by modifying the electrolyte to increase the basicity and/or modifying the cathode materials. Developers are actively investigating both of these options.

2.3. Matrix

The electrolyte matrix provides ionic transport, reactant gas separation and perimeter seal. It is a layer of tightly packed ceramic powder bed impregnated by alkali carbonate electrolyte to form a composite paste-like structure at the operating temperature. The stability of the matrix support materials and matrix robustness (to withstand thermo-mechanical stress) are important considerations that impact the fuel cell performance and endurance. A comprehensive review of the matrix considerations, issues, and status is provided by Yuh et al. [9]. The ceramic $LiAlO_2$ matrix support (a product of the reaction between Al_2O_3 and lithium carbonate) material has three allotropic phases (α, β, and γ). High surface area submicron α-$LiAlO_2$ powder is the current baseline for matrix support material. The material needs to be sufficiently stable in carbonate electrolyte to retain particle size and pore structure for the life goal. An 18,800 h out-of-cell test showed virtually no phase change of the α form. The α-$LiAlO_2$ matrix has shown little change in stability after 18,000 h of operation. During fuel cell stack operation, the matrix experiences both mechanical and thermal stresses. Strong and tough matrices capable of withstanding such stress buildup to maintain good gas sealing capability are desired. Without sufficient strength, the matrix may crack and result in increased gas cross leakage. FCE has developed a cost-effective, strong matrix using an innovative strengthening approach presented by Yuh [10]. This strong matrix has demonstrated no issues with thermal cycleability. Prevention or at least minimization of fuel and/or oxidant leakage or intermixing of the fuel and oxidant is the most important attribute of an operating fuel cell. An intermixing of fuel and oxidant not only reduces efficiency but can also lead to premature component failure due to excessive local heating. The carbonate fuel cell has successfully adapted a simple wet seal concept. Liquid electrolyte held up in the micro-pores of the matrix and on the metal surface where the metal to matrix interface seal is involved, provide adequate barrier to gas leakage.

2.4. Cell hardware materials

In the early years of development, hot corrosion of the metallic hardware (the bipolar separator plate and corrugated current collectors which provide the gas flow passages) in the carbonate environment was an important consideration. Endurance results at FCE and other laboratories have confirmed that a properly selected stainless steel provides adequate corrosion protection for this application. Currently, stainless steels, particularly the 300-series austenitic stainless steels, are the primary hardware materials of the cell stack and BOP (balance-of-plant). Hot corrosion of the bipolar plate and current collector components in the presence of liquid alkali carbonate electrolyte in the two very different hot corrosion environments (reducing fuel and oxidizing oxidant) is considered a major challenge for material selection. Contact electrical resistance could increase due to oxide scale buildup, lowering output voltage. Also, electrolyte loss to the bipolar current collector due to corrosion and electrolyte creepage could further contribute to stack power decay. In general, the anode-side environment (particularly the fuel exit) is more corrosive than the cathode-side, except for pure nickel or high-nickel, nickel-base alloys. The exit condition is generally more corrosive than the inlet due to a higher operating temperature and possibly higher moisture content. Ferritic Al-containing stainless steels have an adequate corrosion rate due to the formation of a dense thin protective inner Cr–Al oxide layer. However, the extremely high electrical resistivity of the alumina-containing scale prevents them from cell active hardware use. For the anode-side application, surface protection of stainless steels by Ni-cladding has generally been adopted. With the protection provided by a nickel-clad coating, the anode-side bipolar plate has shown virtually no corrosion attack during an 18,000 h field operation. Consequently, no significant ohmic loss due to anode-side contact was observed. Although a small amount of chromium-rich oxide forms at the grain boundaries of the nickel-clad layer, no deleterious effect on the corrosion protection is observed. The observed diffusion of iron and chromium from the substrate into the coating appears harmless. The cathode-side current collector (CCC) has a greater corrosion rate than the bipolar plate (BP) because the CCC material selected by FCE has a lower Cr content than BP. Advanced CCC materials that would reduce the corrosion rate, contact resistance increase rate, and electrolyte loss rate are being pursued.

2.5. Wet-seal material

The wet seal simultaneously experiences reducing and oxidizing environments. The chromia-forming alloys experience high corrosion in the wet seal environment. Cost-effective corrosion protection of the wet seal surfaces has been a major focus of materials development efforts. Understanding the corrosion mechanism and as reported by Donado et al. [11], and finding aluminization to eliminate the observed wet seal surface corrosion are considered important steps in carbonate fuel cell development. Aluminizing methods used so far include slurry painting, vacuum deposition, thermal spraying, etc. The resultant diffused coating on stainless-steel surfaces generally consists of
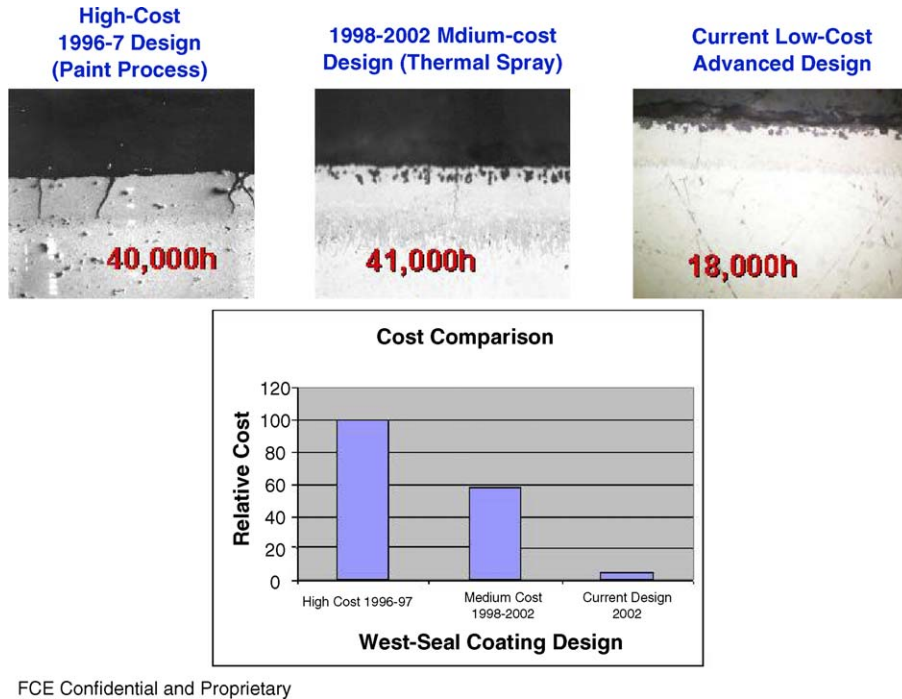
Fig. 6. Wet-seal aluminum protection: through coating advancement, FCE has reduced the cost significantly while maintaining excellent corrosion resistance. >40,000 h life is projected.

a MAl-M$_3$Al structure. The coating has been shown to provide sufficient protection for the substrate stainless steels (Fig. 6), based on long-term >18,000 h testing results. The selected process has very low cost while providing a high-quality diffused coating.

2.6. Power density and thermal management

The electrochemical reactions at the carbonate electrodes are sufficiently fast and account for low polarization losses. Electrode pores have been sufficiently optimized over the years to cause low gas diffusion polarization at current operating power densities (120–140 mA (cm^2)$^{-1}$). There are further opportunities for electrode structure optimization for reduction of cathode gas diffusion polarization as well as internal resistance reduction by electrolyte modification. These efforts are ongoing concurrent with improving temperature uniformity. Operating power density of the large size fuel cells is mainly dependent on thermal management and to a lesser extent on kinetic and gas diffusion polarizations and internal resistive loss. The fuel cell in-plane temperature gradient needs to be managed by employing an efficient cell cooling management system. Currently, the power density-limiting process in the carbonate fuel cell is the cell in-plane temperature uniformity. FCE's direct fuel cell design employs a very efficient thermal management system, where the endothermic internal reforming reaction is used to remove heat generated by the fuel cell. Furthermore, cooling uniformity is achieved by distributing the cell-cooling load between an indirect reformer plate and the direct internal reformer. FCE has developed a comprehensive stack model (that simulates the hydrodynamics, kinetics, electrochemical, and heat trans-
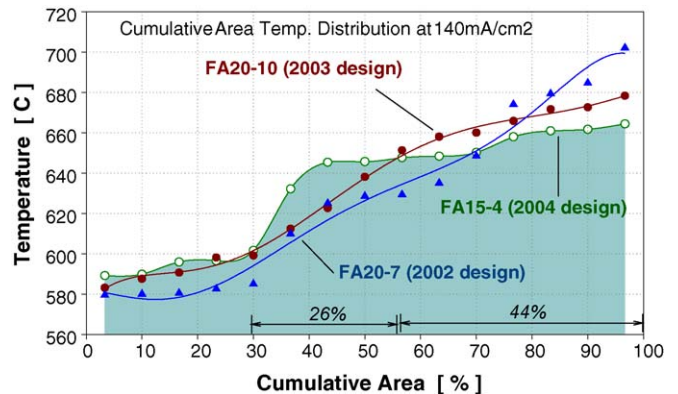

Fig. 7. Area based cumulative thermal distribution in stacks: new RU design significantly reduces cell area above 660 °C.

fer processes) to guide the development of an efficient internal reformer cooling design. As a result, the stack temperature distribution has been improved recently, allowing 20% higher power density operation without incurring penalty in cell temperature gradient. Fig. 7 shows the gradual cell temperature distribution improvement by optimizing the cell cooling design. The internal reformer design has been optimized and as a result the cell temperature uniformity has been increased. As can be seen, the cell in-plane temperature gradient has been reduced from 120 °C in the 2002 design to 75 °C for the 2004 design without sacrificing power density and the cell average operating temperature.

3. Stack design

The commercial cell size of the carbonate fuel cell developers is in the ~1 m^2 (10 ft^2) range, a two orders of magnitude

Fig. 8. Full-size stack completed at the FCE manufacturing facility: ∼350–400 cell stack.

area increase from the early 3 cm^2 cell size during the past three decades. The full-height stack design is different for different developers with respect to gas manifolding and number of cells in the stack. The major characteristics of the carbonate fuel cells are: (1) large cell area, largest among various fuel cell types; (2) high cell area utilization for current production, less than 10% of the geometric area is seal area; (3) ease of fabrication; and (4) lower cost. FuelCell Energy and MTU use approximately 350–400 cells in a full-height 250-kW stack. These stacks are built with the direct-indirect internal reforming concept described by Farooque et al. [12]. A photograph of such a stack, shown in Fig. 8, shows that ∼400 cells are stacked in a bipolar configuration. The Japanese developers have pursued a building block approach. In this approach, a fewer number of cells, typically 80–120 are enclosed within the terminating plates forming a building-block unit. Several of the building-block units are stacked to build a truck-transportable full-height stack.

4. Manufacturing

The carbonate fuel cell employs well-known manufacturing processes. Standard sheet metal forming, bending and welding operations are involved in the manufacture of cell hardware components. The anodes and cathodes are manufactured by standard processing techniques such as tape casting or powder doctoring followed by sintering. Matrix manufacturing by tape casting is also well developed. Most of the developers have demonstrated full-size components manufacture capability. Five developers have already tested full-area cell stacks. At least one developer, FuelCell Energy, currently has 50 MW/year manufacturing capability.

5. Carbonate fuel cell products

Due to its simple system design and high efficiency, several developers around the world are pursuing carbonate fuel

Fig. 9. MTU's hot module is in operation at a factory: an indoor 250 kW unit operating in a industrial environment.

cell products for stationary power generation applications in the near-term and large (10 MW or larger) power plants in the long term. IHI (Ishikawajima Harima Heavy Industries, Co. Ltd.) of Japan has focused on the development of coal-fueled large hybrid power plants based on its pressurized carbonate fuel cell. In the near-term, the company has launched field-testing of 300 kW natural gas units. The first prototype unit was tested in 2003 at Kawagoe, Japan. Additional unit tests on coal gas and biogas have also been planned. A Korean team consisting of KIST (Korean Institute of Science and Technology) and KEPRI (Korean Electric Power Research Institute) is in an early stage of large multi-megawatt systems for coal-gas use. This team is testing a 100 kW system and has a plan to test a 250 kW system in the near-term.

The Italian–Spanish team led by Ansaldo Fuel Cell (AFCO) is focusing on large systems based on its pressurized fuel cell technology. In the near-term, the team is focusing on a 500 kW system. MTU CFC Solutions GmbH of Ottobrunn, Germany has developed a 250 kW stationary fuel cell plant (the HotModule brand) for combined heat and power (CHP) applications. The MTU CFC Solutions plants operating at Bad Berka and Munich in Germany, and at Cartagena in Spain are being used for CHP and air conditioning (trigen). MTU has already placed ten hot module units at customer sites. Fig. 9 shows an indoor hot module operating at the Michelin Karlsruhe, Germany factory. MTU has reported 47% electrical and >80% overall thermal efficiency for their cogeneration system. The sub-megawatt fuel cell power plant is a collaborative effort using the Direct FuelCell® technology of FCE and the HotModule® balance of plant design of MTU CFC Solutions GmbH, a subsidiary of DaimlerChrysler.

FCE is currently commercializing carbonate fuel cell products (DFC Power Plants) for commercial and industrial

customers and continuing to develop the next generation of large size carbonate fuel cell products. FCE's current products, the DFC300A (currently at customer sites, and the enhanced modular design DFC300MA expected to ship to customer site in the fall of 2005), DFC1500 and DFC3000, are rated in capacity at 250 kW, 1 MW and 2 MW, respectively, and are scalable for distributed applications up to 10 MW or larger. These products are designed to meet the base load power requirements of a wide range of commercial and industrial customers including wastewater treatment plants (municipal, such as sewage treatment facilities, and industrial, such as breweries and food processors), telecommunications/data centers, manufacturing facilities, office buildings, hospitals, universities, prisons, mail processing facilities, hotels and government facilities, as well as in grid support applications for utility customers. Through April 2005, over 70 million kWh of electricity has been generated from power plants incorporating the DFC technology at customer sites throughout the world.

The DFC plants have achieved electrical efficiencies of 45–48% in single-cycle applications and have the potential to reach an electrical efficiency 57% at product maturity. In addition, power plants can achieve overall energy efficiency of 70–80% for combined heat and power applications. This is greater than the fuel efficiency of competing fuel cell and combustion-based technologies of similar size and potentially results in a lower cost per kWh over the life of the power plant. Carbonate power plants have significantly lower emissions of greenhouse gases and particulate matter than conventional combustion-based power plants. They emit virtually no NO_x and SO_x and have been designated "ultra-clean" by the California Air Resources Board (CARB).

The carbonate power plants can utilize many fuel sources, such as natural gas, industrial and municipal wastewater treatment gas, propane, and coal gas (escaping gas from active and abandoned coal mines as well as synthesis gas processed from coal).

Biogas offers a unique opportunity for carbonate fuel cells. Industrial wastewater treatment facilities represent a promising market for carbonate fuel cells. The methane produced from the anaerobic digester process is the fuel to generate electricity to power the wastewater treatment plant. The fuel cell heat can be used to heat the sludge to facilitate the anaerobic digestion. Moreover, wastewater treatment gas is a renewable fuel eligible for incentive funding for project installations throughout the world. FCE has fielded several units (two in Japan and four in the US) to operate on digester gas including a 1 MW DFC1500 at King County, WA, USA. The King County unit (photo shown in Fig. 10) operates seamlessly on pipeline natural gas or on the digester gas.

6. Conclusion

While the various fuel cell systems are emerging as new options for power generation, the carbonate fuel cell plants are suitable for high efficiency electricity or combined heat and power for stationary applications. Over 40 units ranging in 250 kW to 1 MW size have been in field operation worldwide. These units have shown 45–48% LHV electrical conversion efficiencies and overall thermal efficiency approaching 80% in CHP applications. The plant emissions are ultra clean. These attributes and the various incentives available for high efficiency, ultra clean renewable fuel technologies are helping market entry of the product in stationary applications. As the technology matures and the cost is lowered through cost-out efforts, the product is expected to capture broader commercial acceptance paving the way for larger multi-megawatt systems.

Acknowledgements

Fig. 10. King county DFC1500 fuel cell power plant: the plant operates on digester gas and on natural gas when digester gas is not available.

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