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# Carbonate Fuel Cell Materials

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**This article reviews the current status and discusses future opportunities for major direct fuel cell (DFC) materials. Major progress on DFC materials development (e.g., electrode, electrolyte, matrix, catalyst, cell hardware, and stack/power plant hardware) at fuel cell energy is discussed. Long-term (i.e., ~18,000 h) field testing results are reported. These results confirm at least a five year operational life for selected key stack materials. Cost reduction is the current main focus.**

**Keywords** fuel cell, high-temperature materials, hot corrosion, molten carbonate fuel cell (MCFC)

## 1. Introduction

Fuel cells are highly efficient and environmentally clean sources of power that are based on electrochemical reactions rather than combustion (Ref 1). The heart of any fuel cell power plant is a fuel cell stack comprising individual cell packages. A schematic of a carbonate fuel cell package is shown in Fig. 1. It consists of two electrodes, anode and cathode, separated by an electrolyte, which in a carbonate fuel cell is a liquid alkali lithium-potassium or lithium-sodium carbonate mixture. The bipolate plate is made of engineered heat-resistant stainless steels. Hydrogen-containing reducing fuel is supplied to the anode; oxygen and $CO_2$-containing oxidant is supplied to the cathode (Table 1). The overall reaction in the carbonate fuel cell is the electrochemical reaction between hydrogen and oxygen to form water (Fig. 2). A carbonate fuel cell is most efficient at temperatures of 550 to 700 °C, which is considered to be an intermediate temperature. This intermediate operating temperature enables the selection of materials from affordable commodity metals.

FuelCell Energy (FCE) has been developing carbonate fuel cell technology for about three decades, culminating in a 2 MW power plant demonstration at Santa Clara, CA in 1996 to 1997. With this valuable experience and further development and scale-up, FCE has delivered more than forty 250 kW DFC300A and one 1 MW commercial power plants during the past few years. Through these, field and endurance technology stack tests, FCE has gathered considerable information on material durability.

## 2. Direct Fuel Cell

Only hydrogen can be efficiently used by fuel cell anodes. Therefore, carbonaceous fuels such as natural gas need to be reformed to generate hydrogen. Carbonate fuel cells operate at temperatures high enough to allow practical reforming reaction kinetics for natural gas and other light hydrocarbons. Therefore, FCE carbonate fuel cell adopts a highly efficient internal reforming fuel conversion approach, as illustrated in Fig. 2.

Designated direct fuel cell (DFC), the thermal and chemical features of the fuel cell, and reforming reactions are designed for efficient integration inside the anode compartment. The overall reaction is simply direct natural gas conversion to water, carbon dioxide, electricity, and heat, without the need for an external reformer. This "one-step" process results in a simpler, more efficient, and more cost-effective energy conversion than possible with external reforming fuel cells. The compact and efficient DFC is ideally suited for stationary distributed generation applications. It is already being commercialized by FCE, and many are already in field service (Ref 2).

A carbonate fuel cell life of five years is required to be commercially competitive. Sufficient long-term stability of stack components against dimensional change (creep), oxidation, and molten salt fluxing attack is required. For the anode and cathode, electrochemical activity is also very important. The materials used presently at FCE have acceptable performance and endurance for commercial use. More importantly, to successfully commercialize the carbonate fuel cell and to compete successfully with other emerging power-generating devices, a low plant cost is necessary.

A review for carbonate fuel cell materials used by developers has been reported on elsewhere (Ref 3). The purpose of this article was to review the current status and to discuss future opportunities for major DFC materials. Major progress on DFC

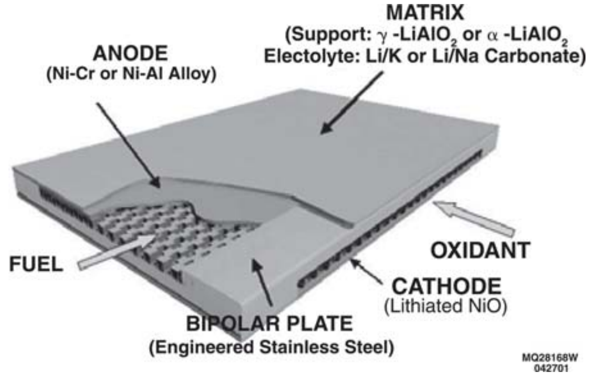

**Fig. 1** A typical carbonate fuel cell package: readily available commodity materials are used.

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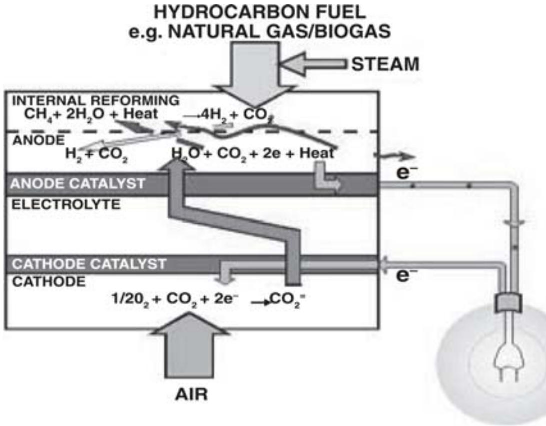

**Fig. 2** Principles of carbonate fuel cell and DFC: efficient heat and mass transfers allow the direct electrochemical conversion of light hydrocarbon fuels.

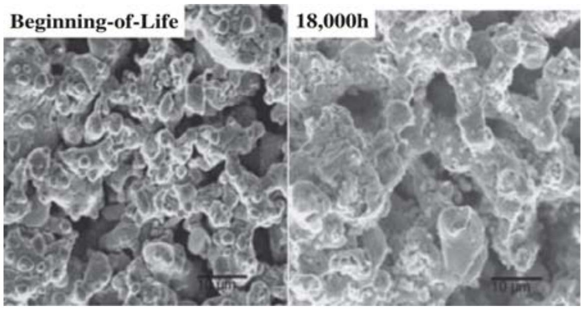

**Fig. 3** Anode after 18,000 h of field service: excellent structural integrity

**Table 1 Anode and cathode environments in carbonate fuel cell**

| Factor | Anode | Cathode |
|---|---|---|
| Atmosphere | Reducing | Oxidizing |
| Oxygen activity | ~$10^{-22}$–$10^{-24}$ | ~0.1 |
| Gas | $H_2$, $H_2O$, CO, $CO_2$, $N_2$ | $O_2$, $H_2O$, $CO_2$, $N_2$ |
| Carbon activity | High (>0.1) | Low (~$10^{-20}$) |

materials development (i.e., electrode, electrolyte, matrix, catalyst, cell hardware, and stack/power plant hardware) at FCE is discussed. Long-term (~18,000 h) field testing results are reported here.

## 3. Anode

Unalloyed porous nickel anodes shrink rapidly under the stack compressive load during operation, resulting in undesired dimensional change, reduced surface area, and lower electrochemical performance. Alloying with Cr and/or Al provides acceptable creep strength, thanks to oxide dispersion strengthening. Excellent mechanical and chemical stability of the baseline DFC Ni-Al anode is verified in an 18,000 h field operation (Fig. 3). Although slight sintering has occurred, the DFC anode showed good structural intergrity and electrochemical activity that can be projected to a >5 year life. Currently, the DFC anode is very cost-effective and only contributes to a very small fraction of the DFC cost, thanks to a successful cost reduction effort by FCE.

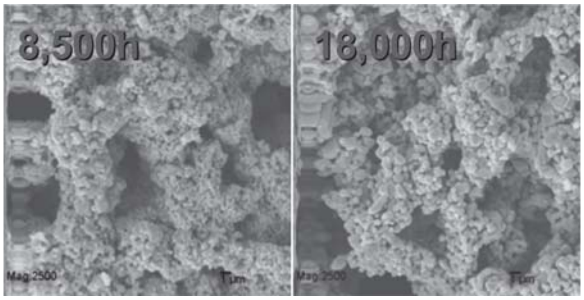

**Fig. 4** A DFC cathode in field operation: only very slight particle coarsening occurred during long-term operation.

## 4. Cathode

The baseline cathode material is lithiated NiO. The extent of its corrosion is controlled mainly by electrolyte composition, applied gas atmosphere, and operation pressure and temperature. FCE selected the approach of operating the DFC under atmospheric pressure to suppress the cathode corrosion/dissolution rate. Long-term field operation has demonstrated quite slow particle coarsening, indicating a very slow and acceptable surface loss rate (Fig. 4). The Ni deposition rate in the electrolyte matrix is also very low, as opposed to those achieved under pressurized operating conditions. The DFC cathode is projected to have a five year operational life under atmospheric pressure operation without Ni shorting.

To reduce cathode corrosion and to increase the cathode lifetime even further, there are in principle two approaches: to modify the electrolyte or to modify the cathode material. The addition of additives has been used to increase the basicity of the electrolyte to reduce the corrosion of NiO. These compounds are added to the fuel cell as a part of the electrolyte or as a component of the cathode material itself. During the past decade, lithium cobaltite seems to have become the most promising substitute for nickel oxide. Because its cost is high, a lower-cost approach is to apply it as a coating to the porous cathode structure. Single-cell experiments at FCE and other organizations showed that the lithium cobaltite coatings reduced the Ni corrosion by a factor of two. In addition to the lithium cobaltite coating, other advanced cathode and electrolyte materials have also been developed by FCE. The life enhancement of the advanced materials has been verified in full-area stacks by FCE, showing a reduced Ni deposition rate and life enhancement by ~2 years. These advanced materials are being incorporated into DFC product stacks.

## 5. Matrix

The electrolyte matrix provides ionic transport, reactant gas separation, and perimeter seal formation. It is a layer consisting of a tightly packed 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 thermomechanical stress) are important considerations that impact performance and endurance.

### 5.1 Support Material Stability

The $LiAlO_2$ matrix support material has three allotropic phases ($\alpha$, $\beta$, and $\gamma$). A high surface area submicron $\alpha$-$LiAlO_2$

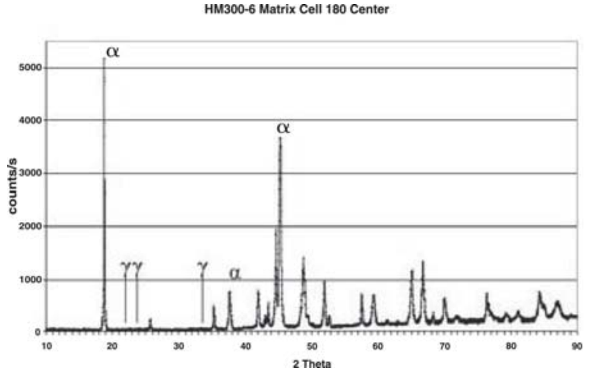

**Fig. 5** Little phase change from the $\alpha$-phase occurs after 18,000 h of field operation. The $\alpha$-phase is selected for product use.

powder is the current baseline DFC matrix support material. Fibers or coarse particulates are also incorporated for strengthening, crack attenuation, and thermal cyclability enhancement. All of these materials need to be sufficiently stable in carbonate electrolyte to retain particle size and pore structure for the intended five year life goal. Long-term carbonate fuel cell testing (up to 34,000 h) revealed significant particle growth and $\gamma$-phase to $\alpha$-phase transformation (Ref 3), which can result in increased mean pore size and pore volume, and in reduced electrolyte retention. The particle grows faster at higher temperatures, in low $\mathrm{CO_2}$ gas atmosphere, and in a strong basic melt. FCE has evaluated the stability of the $\mathrm{LiAlO_2}$ matrices in long-term out-of-cell and stack tests. Significant $\gamma$-to-$\alpha$-phase transformation with associated particle growth near the anode side was observed in a 12,000 h stack that used $\gamma$-$\mathrm{LiAlO_2}$. On the contrary, an 18,800 h out-of-cell test showed virtually no phase change of the $\alpha$-phase. A full-area $\alpha$-$\mathrm{LiAlO_2}$ matrix was successfully used in 250 kW field units at FCE, demonstrating little phase change after 18,000 h (Fig. 5). In summary, the phase stability of the $\alpha$-$\mathrm{LiAlO_2}$ material is sufficient for five years of operation.

### *5.2 Mechanical Strength*

During fuel cell stack operation, the matrix experiences both mechanical and thermal stresses, resulting in the likelihood of matrix fracture. Strong and tough matrices that are capable of withstanding such stress buildup to maintain good gas sealing capability are desired. Without sufficient strength, the matrix may crack along the cell edges and result in increased gas cross leakage. Cell testing has shown that with a proper crack deflector selection, significant improved thermal cyclability can be achieved. FCE has recently developed a cost-effective strong matrix using an innovative strengthening approach (Ref 3). This type of matrix has high strength and toughness, with improved strength during conditioning, after binder burnout before electrolyte filling. This type of matrix has been evaluated at FCE in >500 single cells and in numerous full-area 9000 $\mathrm{cm^2}$ stacks, and has demonstrated excellent beginning-of-life sealing efficiency and thermal cyclability. The advanced matrix has already been incorporated into full-area 250 kW commercial product stacks.

### *5.3 Fabrication*

Faster milling, casting, and drying rates while maintaining consistent matrix quality (>95% yield) are needed. Multiple laminations need to be avoided to reduce processing time and rejection rate. Matrices as wide as 1 m have been manufactured for the product power plants. FCE has developed a fast matrix manufacturing method that reduced the production time by two thirds. Cost reduction (i.e., for raw materials, matrix thicknesses, and processes) is the current major focus. A significant cost reduction for the $\alpha$-$\mathrm{LiAlO_2}$ raw material (by 50%) has recently been achieved. It is estimated that the current $\alpha$-$\mathrm{LiAlO_2}$ cost is still >10 times the cost of raw materials (e.g., $\mathrm{Li_2CO_3}$ or $\mathrm{Al_2O_3}$) and can be explained by the slow manufacturing processes currently being used (e.g., batch process, long process time, or low yield). Therefore, alternate low-cost manufacturing methods for $\alpha$-$\mathrm{LiAlO_2}$ need to be developed.

## 6. Cell Hardware Materials

Metallic heat-resistant alloys are extensively used and are subjected to oxidation and/or hot corrosion (molten salt fluxing attack). Currently, stainless steels, particularly austenitic stainless steels, are the primary hardware materials of cell, stack, and balance of plant (BOP).

### *6.1 Bipolar Current Collector Materials*

A bipolar current collector consists of a bipolar plate (BP) and current collectors (Fig. 1). Hot corrosion of this component in the presence of a liquid alkali carbonate electrolyte in the two very different hot corrosion environments (i.e., reducing fuel and oxidizing oxidant) is 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 fuel exit) is more corrosive than the cathode-side environment, except for pure Ni, or high-Ni and Ni-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 adequate corrosion rates 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, the surface protection of stainless steels by thermodynamically stable Ni coatings has generally been adopted by developers. Electrolytic Ni plating (e.g., a sulfamate bath) produces a very pure Ni coating but with nonuniform thickness distribution on current collectors of corrugated shapes. Furthermore, the electrolytic Ni structure is not as dense as the Ni-clad layer. With the protection provided by a Ni-clad coating, the anode-side BP has shown virtually no corrosion attack during an 18,000 h field operation (Fig. 6). Consequently, no significant ohmic loss due to anode-side contact was observed. Although a small amount of Cr-rich oxide forms at the grain boundaries of the Ni-clad layer, no deleterious effect on corrosion protection is observed. The diffusion of Fe and Cr from the substrate into the coating appears tolerable. However, to avoid the high cost of the Ni coating, FCE has successfully identified advanced low-cost, heat-resistant alloys that showed adequate anode- and cathode-side corrosion resistance that can be projected to a >5 year operational life (Fig. 7).

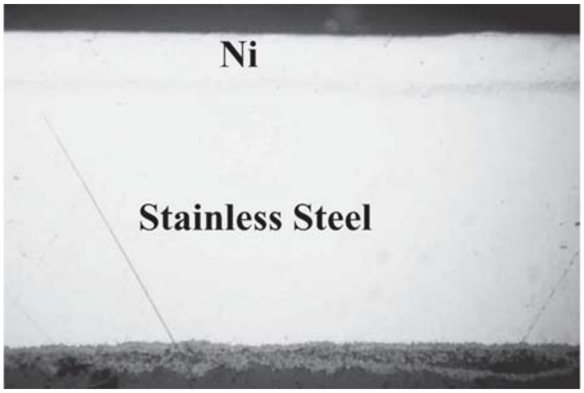

**Fig. 6** After 18,000 h, the Ni coating provided excellent protection to a stainless steel substrate. The stainless steel substrate also provided adequate cathode-side corrosion protection.

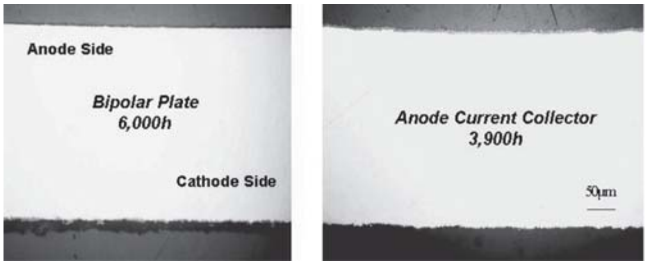

**Fig. 7** Excellent corrosion resistance of an advanced alloy demonstrated for BP and anode current collector

The cathode current collector (CCC) has a faster corrosion rate than the BP (Fig. 8) because the CCC material selected by FCE has a lower Cr content than the BP. To reduce this CCC corrosion, FCE has developed advanced CCC materials that reduced the corrosion rate, the contact resistance increase rate, and the electrolyte loss rate (Fig. 9). The materials are being scaled up for product use.

### 6.2 Wet-Seal Material

The wet seal simultaneously experiences reducing and oxidizing environments; chromia-forming alloys experience high corrosion. Only alumina-forming alloys are acceptable in such an environment. Because it is difficult and expensive to manufacture a bipolar current collector incorporating a bulk aluminum-containing alloy at the wet-seal area, an aluminized coating has generally been selected.

The aluminizing methods used so far include slurry painting, vacuum deposition, and thermal spraying. The resultant diffused coating on a stainless steel surface generally consists of an MAl-$M_3$Al structure. The coating has been shown to provide sufficient protection for the substrate stainless steels (Fig. 10), based on long-term >18,000 h testing results. The current selected process has a very low cost while providing a high-quality diffused coating. Based on these results, it is projected that the stability of the selected coating is adequate for five years of use.

## 7. Stack and Balance of Plant Hardware

The life goals for the nonactive stack hardware and BOP materials are five and 30 years, respectively. These materials are not in the path of current conduction and are not in direct contact with the liquid electrolyte; the electrical conductivity of the oxide scale is not required. Only oxidation resistance and scale spallation behavior are important. The oxide spallation behavior is particularly important for components near the stack because the spalled debris may block the gas flow passage and may also compromise the stack electrical isolation. Another important consideration is the cost. Currently, BOP materials contribute to a significant portion (i.e., >65%) of the total power plant cost. Therefore, high-cost materials such as superalloys are only used for a few components that experience very high stresses or a high corrosion environment.

FCE has accumulated significant experience with the long-term stability of high-temperature metallic alloys from out-of-cell and stack testing, with test durations up to 18,000 h. A

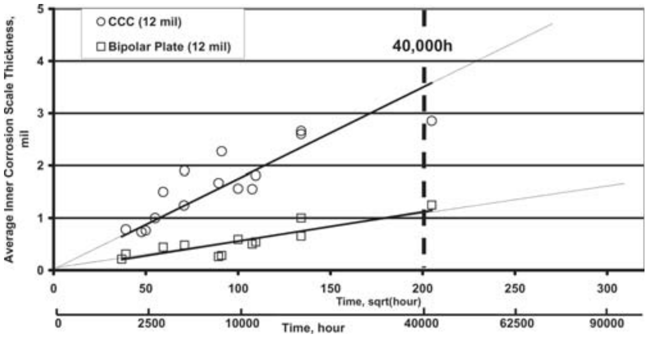

**Fig. 8** Corrosion rate of the CCC is faster than that for the BP. The BP material has a higher Cr content.

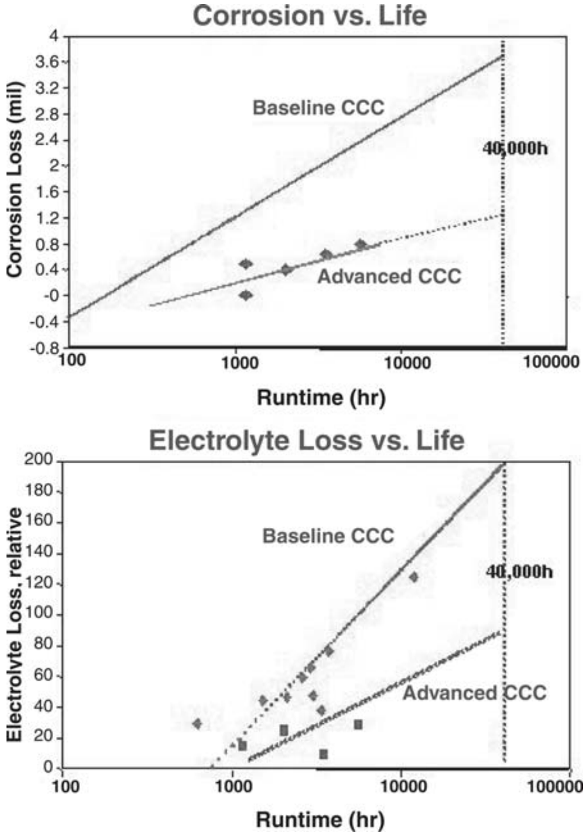

**Fig. 9** The advanced CCC material significantly reduces corrosion and electrolyte loss of the CCC.

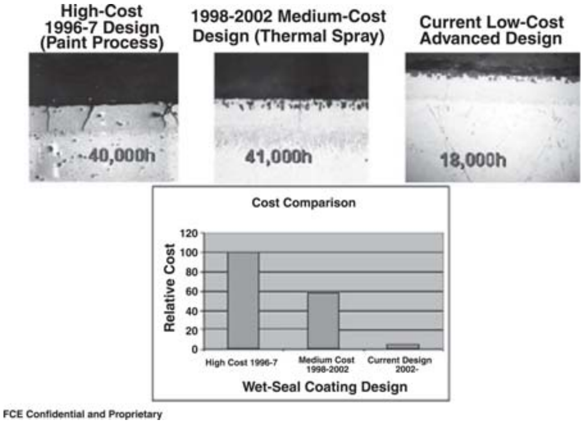

**Fig. 10** Wet-seal aluminized coating: through coating advancement, FCE has reduced the coating cost significantly while maintaining excellent corrosion resistance. A >40,000 h life is projected.

series of accelerated thermal cyclic oxidation tests in an oxidizing atmosphere at 700 °C conducted by FCE show that both SS316L and SS321 experience high oxidation rates and high spallation, which are inadequate for the life target (Fig. 11). In general, SS304 is better than SS316 in terms of both oxidation rate and spallation. SS310S, 18SR, and 253MA, having either high Cr content or containing Al or Ce, have excellent oxidation resistance in the oxidant environment. SS347 has superior oxidation resistance and adhesion due to a very fine grain structure.

To further evaluate alloy oxidation behavior under various conditions (e.g., fuel-in, fuel-exit [F/E], oxidant-in, and oxidant-exit), numerous alloy samples were placed in various locations in the stacks at FCE during testing. A test duration up to 15,000 h has been accumulated. In general, oxidation in the exit condition is more severe than that in the inlet condition, probably due to the higher exit temperature, higher water partial pressure, as well as the presence of alkali carbonate vapor. The F/E environment is more corrosive than that on the oxidant side due to a less passive oxide scale formation. The test further verified the results from the out-of-cell accelerated thermal cycling testing. The oxidation rates of SS321 and SS316L are about 10 times as high as that of SS310S and about five times as high as that of 18SR. Based on the test results, alloys with balanced Fe, Ni, and Cr can be selected for various stack hardware.

For the power plant BOP, a relatively thick-walled 300 series authentic stainless steel is usually used. Spallation of the corrosion scale is the major consideration. SS304L has been tested at various locations in the facility pipes of the FCE stack testing station and a 1.8 MW Santa Clara demonstration power plant. It is found that the lower Cr content of SS304L or SS304 is adequate for the thick-walled piping application. The $Al_2O_3$-forming ferritic stainless steels, having a very low oxidation rate and high scale spallation resistance as described earlier, may be used in areas where debris formation needs to be avoided.

## 8. Internal Reforming Catalyst

In the DFC concept, the fuel cell and reforming reactions are carried out in close proximity to allow rapid thermal and mass exchanges. In the conventional DFC approach, called direct internal reforming (DIR), the catalyst is located in the anode compartment where it gets exposed to the electrolyte-containing environment. An alternate approach, called indirect internal reforming (IIR), in which the reforming catalyst is placed in between cell groups and is not exposed to carbonate vapor, is able to achieve a much longer catalyst life while retaining thermal management benefits. A hybrid system incorporates both.

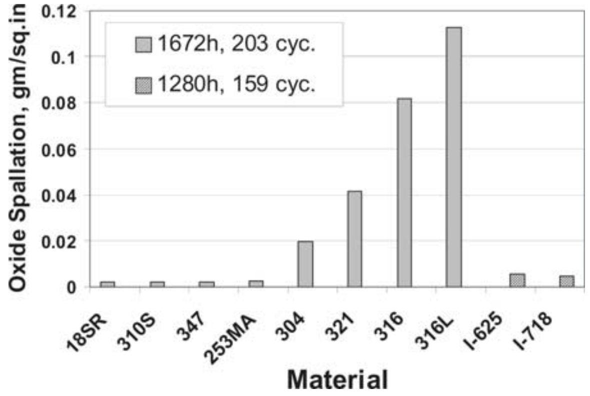

**Fig. 11** Accelerated thermal cyclic oxidation testing under oxidizing atmosphere (between room temperature and 700 °C): 18SR, SS310S, SS347, and 253MA all showed excellent cyclic oxidation resistance.

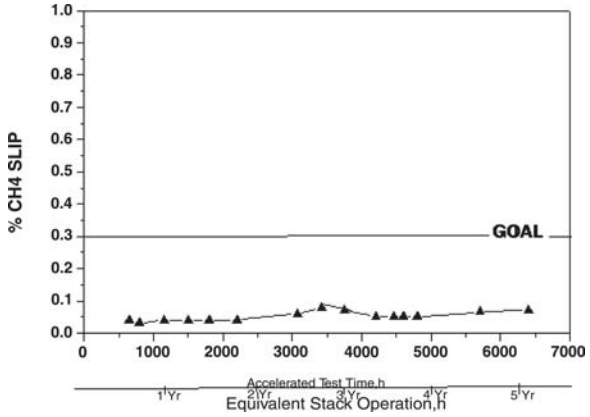

**Fig. 12** An advanced DIR catalyst showed excellent reforming stability in 6500 h single cell testing. The catalyst also has a verified adequate life in product testing.

The conventional reforming catalysts have shown negligible deactivation in IIR. On the other hand, the stability of the DIR catalyst is strongly affected by the fuel cell environment. The major causes for the deactivations of the DIR catalyst are: electrolyte contamination; catalyst sintering; and irreversible catalyst poisoning due to the presence of sulfur impurities in the feed gas. Conventional high-temperature sintering is not considered to be the root cause of decay due to the somewhat low carbonate fuel cell operating temperature (~650 °C). This leaves the electrolyte as the major contributor. Electrolyte creepage toward the catalyst has been resolved by utilizing a nonwetting metal surface like Ni for the anode-side hardware. Hence, current DIR catalyst deactivation is mainly achieved by vapor phase transport. This process results in poisoning of the active sites as well as structural deterioration. Electrolyte pickup by the catalyst results in decreasing active metal and surface areas. Active metal sites were further decreased significantly as a result of possible accelerated sintering in the presence of an electrolyte. In addition, pore filling/plugging of the catalyst support and coverage of the active metal sites by the electrolyte vapor may further contribute to the overall deactivation. FCE has selected a more stable and active DIR catalyst. Figure 12 showed the reforming results of a bench-scale DFC single cell, indicating little methane slippage and stable catalyst activity for 6500 h. The advanced catalyst has been used in DFC product stacks and is projected to provide more than five times longer life compared to the prior baseline catalyst. It is projected for >5 years of use.

## 9. Summary and Outlook

Major progress on DFC materials development (i.e., electrode, electrolyte, matrix, catalyst, cell hardware, and stack/power plant hardware) at FCE has been reviewed. Long-term (~18,000 h) field testing results confirm the five year operational life of selected key stack materials. Cost reduction is the current main development focus.

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