

Review Paper

Status of carbonate fuel cell materials

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Abstract

Issues, status and selection considerations for carbonate fuel cell anode, cathode, matrix and bipolar current collector materials have been reviewed. The presently used materials have adequate performance and endurance for large-scale demonstration. Cost reduction is desired for successful commercialization and is the current research focus. Opportunities for further beneficial performance and endurance improvements have been identified in this paper.

Keywords: Carbonate fuel cell materials

1. Introduction

Carbonate fuel cell is a highly efficient and environmentally clean source of power generation [1,2]. Many organizations worldwide are actively pursuing the development of this technology. Significant progresses in research and development have been achieved during the past quarter century. Consequently, field demonstration of multi-MW size power plant will be initiated in 1995–1996 [3], a step toward commercialization before the turn of the century.

The heart of the carbonate fuel cell power plant is the d.c. power block. The power block comprises multiple fuel cell stacks, identical in construction. A fuel cell stack consists of individual fuel cell packages stacked together. A schematic of a cell package is shown in Fig. 1. Carbonate fuel cells are operated at 600–700 °C in the presence of corrosive liquid Li/K carbonate in both reducing (high carbon activity) anode and oxidizing cathode atmospheres. Sufficient long-term stability of stack components against dimensional change (creep), oxidation and molten salt fluxing attack is a

major consideration for material selection. For economical generation of power, a useful cell life of 25 000–40 000 h is desired. For anode and cathode, electrochemical activity is also a very important consideration. Although materials used presently have acceptable performance and endurance, advanced materials that can further increase performance and extend life (to well beyond the present 40 000 h) will be very beneficial, to accelerate the commercialization. More importantly, to successfully commercialize the carbonate fuel cell and to compete successfully with other emerging power generating devices (e.g., gas turbine), stack cost reduction is desired. In fact, stack cost reduction is the current primary challenge in stack research for many developers, besides scale-up and demonstration. In this paper, status of some important carbonate fuel cell components (anode, cathode, matrix and bipolar current collector) is reviewed and improvement opportunities to achieve the above performance, endurance and cost goals are discussed (as summarized in Table 1).

2. Anode materials

Nickel has been used as the anode material for the past two decades. It has been shown to have good electrochemical activity with measured polarization loss less than 30 mV at 160 mA/cm² [4,5]. Therefore, prior major research effort has been to strengthen the nickel anode [6,7]. Without strengthening, a porous nickel anode would shrink (creep) significantly under stack compressive load during operation (> 50% thickness decrease in only several days). This cre-

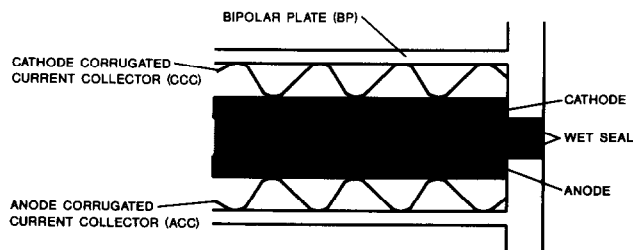


Fig. 1. Schematic of the carbonate fuel cell: cell components exposed to high-temperature hot-corrosion environment.

Table 1
Carbonate fuel cell: present materials and potential improvements

Component	Present materials	Potential improvements
Anode	Ni–Al, Ni–Cr	Alternate materials, low-cost processes, less materials
Cathode	NiO	Alternate materials or electrolytes
Matrix	Reinforced LiAlO ₂ powder bed	Advanced reinforcements
Separator	Ni coated 310S/316L, aluminizing	Single-alloy materials, low-cost coating processes

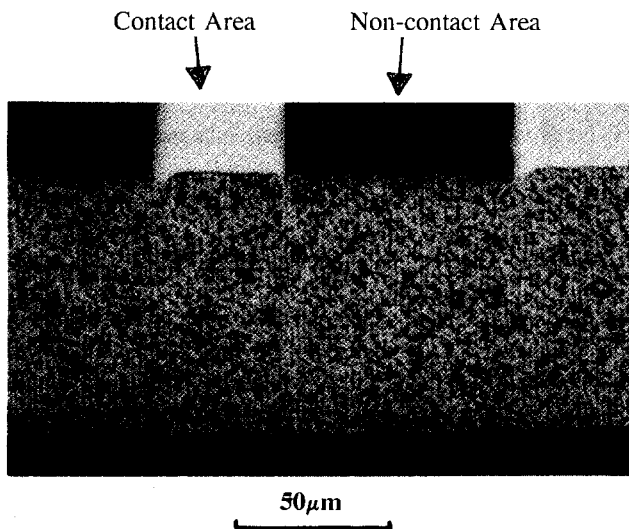


Fig. 2. Oxide-strengthened Ni–Al anode after 7000 h testing: creep strength appears acceptable.

ates significant mechanical stress and contributes to matrix cracking. Furthermore, anode surface area decreases and electrochemical performance also suffers. Impregnation of LiAlO₂ has been shown to improve creep strength, although still not sufficient for 40 000 h use [6,8]. The use of nickel-coated ceramic precursor powders has achieved the desired creep strength [9] but the de-lamination of the nickel layer during long-term operation is a concern. The nickel anodes sintered from Ni–Cr and Ni–Al alloyed powders has shown acceptable strength thanks to oxide dispersion strengthening [7,8,10,11] and are the current choices for commercialization. Figs. 2 and 3 showed little changes of Ni–Al anode thickness and morphologies after 7000–10 000 h stack operation.

However, the present baseline anode contributes to about 30% of the stack material cost based on ERC's (Energy Research Corporation) cost study; research to reduce anode cost is important for commercialization. Cost reduction could be achieved by using alternative low-cost anode materials, reducing the quantity of material used, and improving manufacturing methods.

Doped MnO, CeO₂ and LiFeO₂ materials have been evaluated recently [12,13]. So far, anodes made from the above materials showed performance considerably less than the baseline Ni–Cr anode. Low performance could be caused by low intrinsic electrochemical activity or not yet optimized pore structure. Pure LiFeO₂ has been shown kinetically unfavorable [14]. It was suggested that with proper doping CeO₂ may give a performance equivalent to the Ni–Cr anode [13]. However, post-test analysis showed that all of the above alternate materials suffered some chemical instability. It is not assured if the above materials have the stability for 40 000 h use. Cu–Al anodes (electrochemical activity similar to nickel) have also been evaluated, but without much success in terms of creep strength so far [15]. Recently, Cu–Ni–Al alloy anode has been shown to have equivalent creep strength and electrochemical performance as Ni–Cr [16]. It should be noted that if copper is made a successful anode material, anode-side nickel coating may need to be replaced by copper to alleviate the problem caused by the fast interdiffusion between nickel and copper [17]. It may be pointed out that if copper is used in the fuel cell, then the salvage value of the stacks would be downgraded significantly.

Other approaches for cost reduction include reduced material use or alternate manufacturing methods. Because of the fast electrochemical activity of nickel, reduced material use

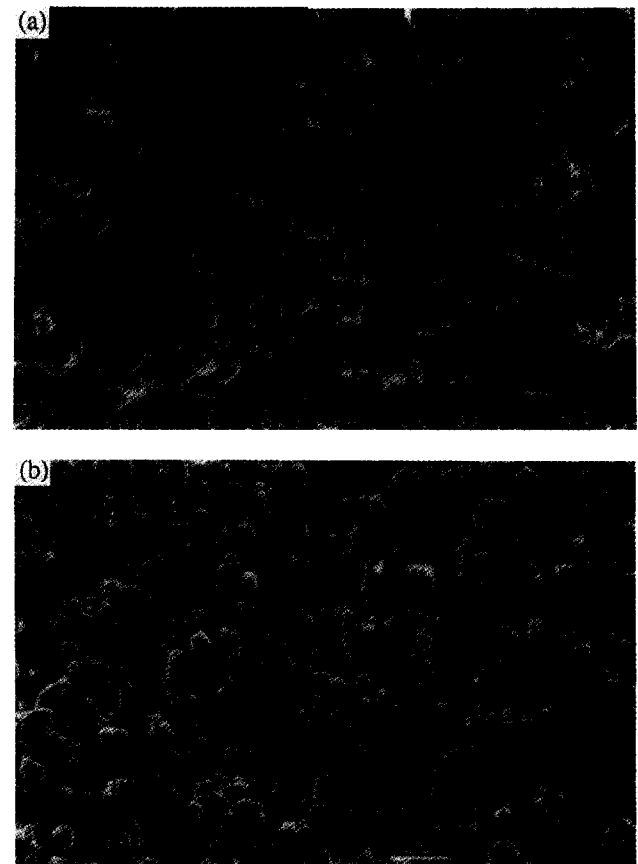


Fig. 3. Morphologies of oxide-strengthened Ni–Al anode: no significant change of morphologies: (a) as sintered, and (b) after 10 000 h testing.

may not cause reduction of performance [18]. Alternate manufacturing methods to reduce raw powder cost as well as manufacturing processing cost will also be very desirable.

3. Cathode materials

The NiO has been the choice of the cathode material since the 1970s [19]. NiO cathode generally forms by in situ oxidation of porous nickel during cell start-up. The NiO cathode formed this way has a dual-porosity structure providing both gas accessibility as well as ionic transport path. The electrochemistry at NiO surface and rate-limiting processes in the porous NiO electrode have been studied by various researchers [20–22]. Although the fundamental electrochemical reaction mechanisms have not yet been clearly elucidated, the measured electrochemical activity was clearly one order of magnitude lower than the anode. Including diffusional and ohmic polarization losses, the present porous NiO cathode is projected to cause ~ 100 mV total polarization loss at 160 mA/cm². Although this loss is acceptable now for field demonstration, its further reduction is desired. Further improvement in electrochemical performance will require a better understanding of fundamental reaction mechanisms as well as the effect of pore structure; material improvement, pore structure optimization and electrolyte modification are possible approaches. At present, reduction of NiO corrosion is the primary research focus.

3.1. NiO corrosion

The corrosion of the NiO cathode is one of the important issues in carbonate fuel cell research [23–30]. Significant amount of metallic nickel in the electrolyte structure was first discovered in 1981, in a pressurised (10 atm) UTC cell, later confirmed by other developers [19]. The NiO has a low equilibrium solubility of < 30 wppm in carbonate melts. The dissolved nickel ions precipitate as the nickel metal when they encounter more reducing atmosphere near the anode. The concentration gradient thus produced provides the driving force for NiO transport, with net result of continuous cathode dissolution and nickel precipitation in the matrix [24,25]. Thus, NiO dissolution/deposition can cause two problems: cathode material loss and cell internal shorting. ERC has found that a 750 μm cathode may lose up to 40% of its total mass in nickel and still functions within the desired performance limit [11]. Therefore, a more important life criterion is the maximum allowable cell internal short-circuiting current density. The short-circuiting current results in parasitic fuel loss as well as cell voltage loss. A short-circuiting current of 10 mA/cm² translates to about 2.5% loss in overall efficiency.

It has generally been agreed that the NiO cathode dissolves by acidic mechanism and an increase in melt basicity reduces solubility. However, other cell operating factors such as cathode polarization may affect dissolution rate [26,27]. A model

developed by Shores et al. [27] can satisfactorily predict the transport rate, but it needs to be modified to predict the advancement of deposition boundary and the spreading of nickel deposition zone, generally observed in post-test matrices [28,29]. This spreading has been simulated by a nickel chain growth model, assuming nickel ion transport as the rate-limiting step [29]. The spreading of the nickel deposits may also be partly due to inhomogeneities in the matrix. Although there are disagreements regarding the exact correlation for cathode loss versus time [8,28], probably due to the different types of matrix structures and operating conditions used by different developers, it is generally agreed that a CO₂ lean cathode gas and more basic melts can suppress NiO loss rate. However, the nickel deposition rate cannot be used confidently to predict cell life to short, which is also greatly affected by nickel deposition pattern and location.

Another important phenomenon that was only recently emphasized is the segregation of electrolyte composition in the matrix under the effect of electric potential. Li/K segregation in cells may cause a dissolution rate more than that predicted under equilibrium conditions [30]. SrCO₃, a basic additive to suppress NiO solubility, was also found to segregate near the anode during operation [30], causing a diminished capacity in suppressing NiO dissolution. Research efforts to find basic non-segregating electrolytes will be very beneficial.

The effect of nickel deposition on time to short has been studied extensively [26,31]. The time to short was found proportional to matrix thickness and inversely proportional to NiO solubility. A 40 000 h life is achievable, using a thick matrix, operating under low CO₂ partial pressures (~ 0.1 atm) and at -100 mV cathode polarization with respect to a 33O₂/67CO₂ reference electrode [26]. It was also observed that shorting appeared localized, probably along defect structure. Therefore, a uniform homogeneous noncracking matrix structure is desired to eliminate preferred Ni deposition locations. Because localized shorting is expected to be strongly affected by matrix structure, different research organizations may find different time to short because of the different matrices used. Nevertheless, using a reported correlation [31], a short-circuiting life of 40 000 h can be projected by using thick, uniform and noncracking matrix (> 750 μm thick), a CO₂ lean (< 0.15 atm) cathode gas and a basic, nonsegregating electrolyte. However, for pressurized stack operation, nickel shorting may still be a concern.

At present 6000–10 000 h of cell life have been demonstrated in several multi-cell stacks at ERC without failures caused by cathode dissolution. Furthermore, post-test analysis of the NiO cathode, after 10 000 h stack operation under a CO₂ lean cathode gas, did not show significant changes of surface area or morphology (Figs. 4 and 5). Therefore, ERC believes that cathode corrosion is fairly manageable for atmospheric-pressure stack operation. Nevertheless, fundamental research (e.g., understanding the spreading phenomena of nickel deposits) to further extend fuel cell life or improving reliability will be beneficial.

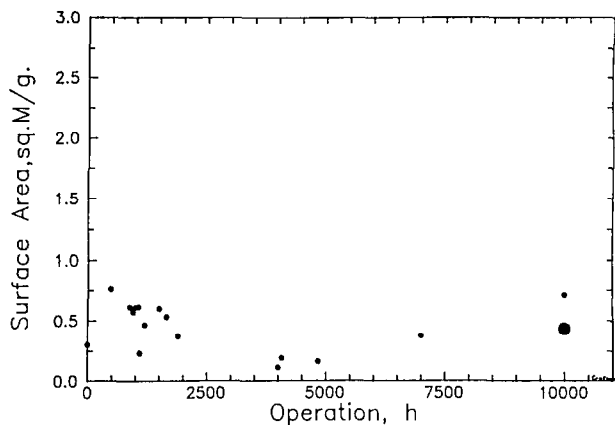


Fig. 4. NiO surface area change after 10 000 h testing: cathode surface area is stable.

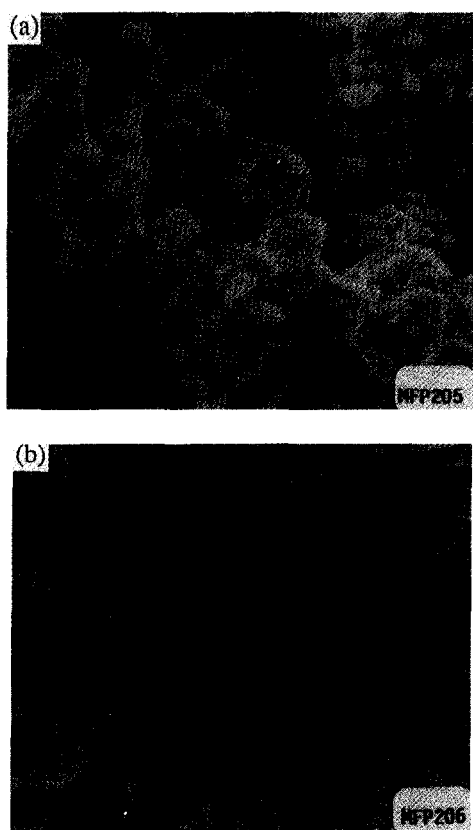


Fig. 5. Stability of NiO cathode: no significant change of NiO particle size after (a) 1000 h testing, and (b) 10 000 h testing ($\times 1670$).

3.2. Alternate cathode materials

Several alternate cathode materials (doped LiFeO_2 and Li_2MnO_3 , and LiCoO_2) are being evaluated to substitute NiO [12,13,32,33], mainly to alleviate the concern of cell shorting associated with NiO dissolution. LiFeO_2 and Li_2MnO_3 do not deposit as metal in matrix. LiCoO_2 does deposit as cobalt metal but probably at a smaller quantity than nickel [32] and mostly in anode [34]. So far, the electric conductivities of these cathode materials have been significantly improved by

doping and may be considered acceptable. However, porous cathode performance is usually lower than the baseline NiO, likely due to unoptimized pore structure. Recently, the use of pore former has improved LiCoO_2 performance significantly [35]. Although the desired performance is achieved, long-term endurance testing is required to determine stability and life to shorting.

4. Matrix materials

The matrix is a key component in carbonate fuel cell, providing ionic transport, reactant gas separation and perimeter seal formation. All developers are using a tightly packed ceramic bed impregnated by electrolyte to form a paste-like structure. Submicron $\gamma\text{-LiAlO}_2$ powder has been used as the major ceramic material due to its chemical inertness. The current development efforts focus mainly on optimizing the matrix structure and scale-up of the manufacturing process [36].

Tape casting method has been selected as the commercial manufacturing process for cost-effective fabrication of full-area thin matrices. Matrices as wide as one meter have been manufactured at a manufacturing rate of several MW per year. Process and equipment optimization is required before the transition can be made from pilot to commercial manufacturing of several hundred MW per year capacity. Faster casting and drying rates will be needed. Slurry systems may need modifications to accomplish this.

During fuel cell stack operation, the matrix experiences both mechanical and thermal stresses. Different mechanical characteristics of active and wet seal areas generate mechanical stress. Thermal stress is generated by nonuniform temperature distribution and by thermal cycling. Furthermore, large change in electrolyte volume associated with freezing/melting generates additional stress. The composite of ceramic particles and electrolyte (liquid or frozen) may not be sufficiently strong to withstand the stress buildup. Cracking of the matrix resulting from the above causes can result in gas leakage increase, lower efficiency, shorter life and poor power plant efficiency. Therefore, strong and tougher matrices to maintain good gas sealing capability is highly desirable.

A matrix formulation that improves matrix sealing efficiency and thermal cycleability was developed at ERC [37] (Fig. 6). As an example, the 4000 cm^2 area stack AF-2-11 was thermally cycled six times with only a small increase of leakage during its 6000 h testing. Nevertheless, further reduction of this small increase of leakage with each cycle will require stronger and tougher matrices.

Literature survey has shown that crack deflectors of various shapes can be used to reinforce ceramic composite [38]. Cell testing has shown that with a proper crack deflector selection, significant improved thermal cycleability can be achieved (Fig. 7). In terms of crack deflection effectiveness, fiber is the most effective, followed by platelet. Spherical boulder is the least effective. Ceramic fibers are being studied exten-

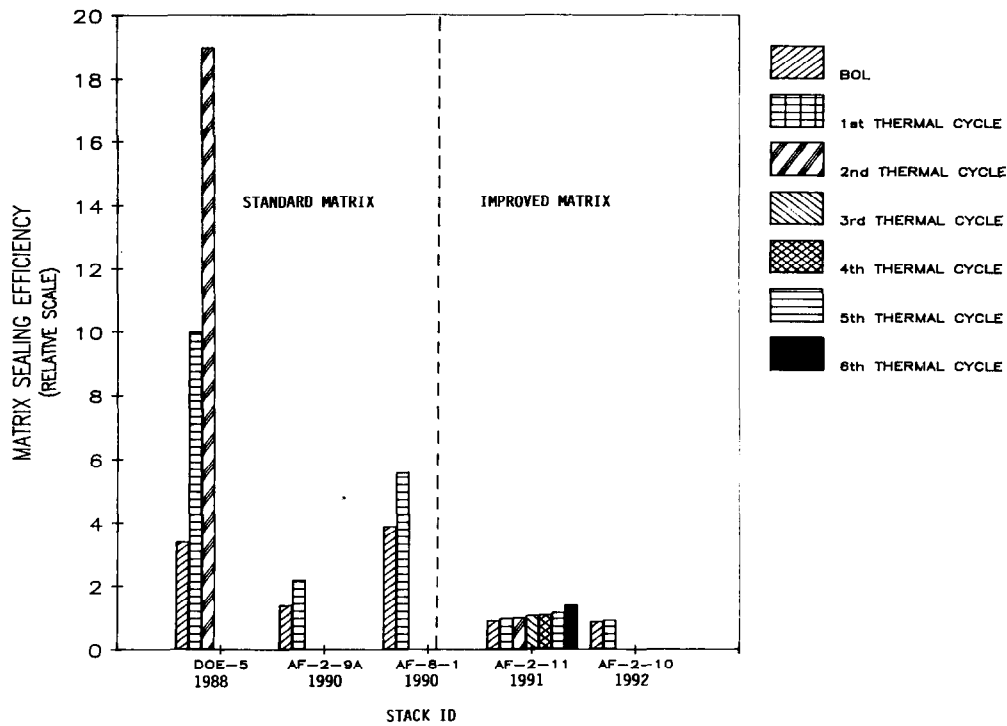


Fig. 6. Improved thermal cycleability achieved in stack tests with improved matrix formulation.

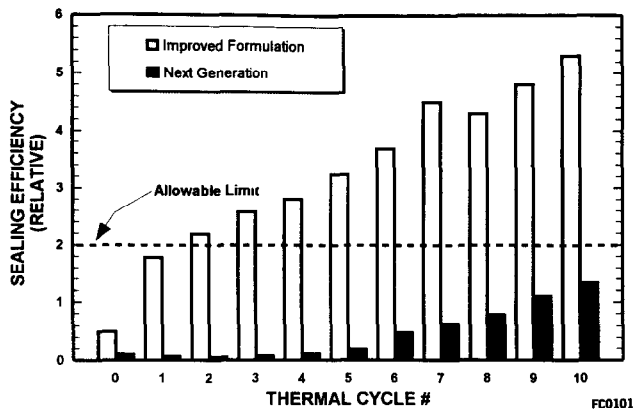


Fig. 7. Thermal cycleability of matrix with advanced reinforcement: significant improvement in thermal cycleability achieved using advanced reinforcement.

Table 2
Anode and cathode environments in carbonate fuel cell: two very different environments in carbonate fuel cell

	Anode	Cathode
Atmosphere (oxygen activity)	Reducing (~10 ⁻²² -10 ⁻²⁴)	Oxidizing (~0.1)
Gas species	H ₂ , H ₂ O, CO, CO ₂ , N ₂	O ₂ , CO ₂ , H ₂ O, N ₂
Carbon activity	High (~0.2-0.3)	Low (~10 ⁻²⁰)

sively for reinforcing ceramic composites. Available choices of high-temperature ceramic fibers for carbonate fuel cell use are rather limited due to the high corrosivity of carbonate.

SiC fiber commonly used in composite industry is unstable in molten carbonate. Commercially available γ -LiAlO₂ fiber is defective and weak in structure. The incorporation of the above fibers has not achieved sufficient matrix strength improvement. The long-term stability of commercial alumina fiber is questionable due to carbonate attack, preferentially at glassy grain-boundaries if sintering aid such as silica is used. Even high-purity alumina fiber made by sol-gel process may not have sufficient corrosion stability for 40 000 h in carbonate. Therefore, fiber reinforcement approach can be employed only after strong and stable ceramic fibers become available.

5. Bipolar current collector

A bipolar current collector consists of bipolar plate and current collectors (Fig. 1). Hot corrosion of this component in two very different hot corrosion environments (Table 2) presents a challenge to material selection. Hot corrosion attack impacts mechanical properties of current collectors, accelerates electrolyte loss and contributes to ohmic resistance increase. Therefore, a slow corrosion attack is desired for 40 000 h stack operation.

About sixty different high-temperature alloys, including Ni-, Co- and Fe-base chromia- or alumina-forming alloys, have been evaluated so far (Table 3) by various developers [26,39-41]. The materials were mostly evaluated in out-of-cell corrosion testing. In general, the anode-side environment is more corrosive than the cathode-side, except for pure nickel or high-nickel nickel-base alloys (e.g., Inconel 600).

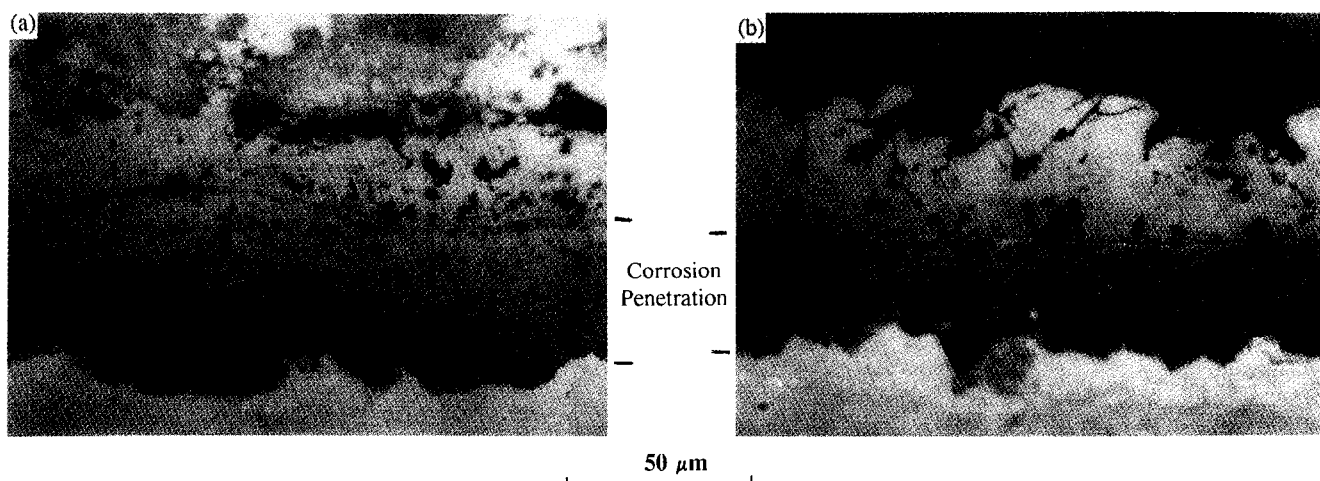


Fig. 8. Hot corrosion of ferritic stainless steel in anode environment (650 °C, 1000 h): corrosion resistance is unacceptable (a) SS430 (16% Cr), and (b) SS446 (25% Cr).

Table 3

Alloys evaluated by various developers ^{a,b}

Iron-base alloys

304L, 309S, 310S, 314, 316L, 347, 405, 430, 446, 17-4PH
18-18⁺, 18SR, A118-2, A126-1S, A129-4, A1439, Glass Seal 27,
Ferrallium 255, RA253mA, Nitronic 50, 20Cb3, 330, Crutemp-25,
Crutemp-25 + La, Sanicro-33, 310 + Ce, IN800, IN840, A-286

Nickel, cobalt-base alloys

IN600, IN601, IN671, IN690, IN706, IN718, IN825, IN925, MA956,
RA333, Ni200, Ni201, Ni270, Haynes 230, Haynes 625, Haynes 188,
Haynes 556, Nichrome, Monel 400

Aluminum-containing alloys

GE-2541, FeCrAl + Hf, Haynes 214, Fecralloy, IJR (406), 85H,
Kanthal AF, Ni₃Al

^a IFC, GE, IGT, IITRI and ERC.

^b About sixty different alloys evaluated so far.

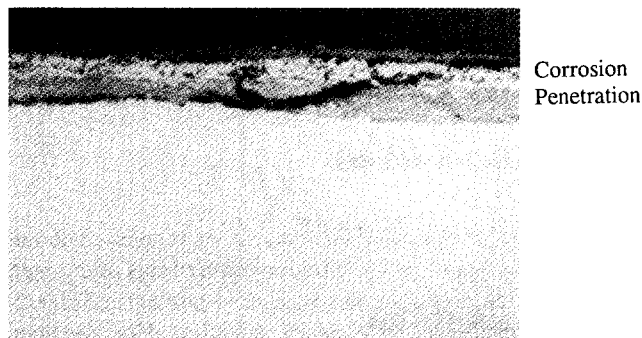


Fig. 9. Hot corrosion of nickel-base alloy RA333 45Ni–35Cr in anode environment (700 °C, 1000 h): corrosion resistance is not sufficient ($\times 140$).

The high-chromium (Cr > 18%) Fe–Cr ferritic stainless steels are low cost but not sufficiently corrosion resistant in both the anode and cathode environments (Fig. 8). The nickel-base high-temperature alloys with nickel content less than 50% (e.g., RA333, Incoloy 800 or 825) perform slightly better than stainless steel in the cathode environment, but still not acceptable for anode-side use (Fig. 9). Furthermore, many nickel-base alloys contain molybdenum, tungsten,

niobium, titanium, etc. for strengthening. These alloying elements are considered detrimental for hot-corrosion resistance. Only high-nickel nickel-base alloys (e.g., Inconel 600 with 75% Ni) has acceptable anode-side corrosion resistance [41] (nickel is thermodynamically stable); however, these alloys are expensive and not sufficiently corrosion resistant in the cathode environment.

The Fe–Ni–Cr austenitic stainless steel 310S and 316L are the current choices for their acceptable cathode-side corrosion resistance and relatively low cost. However, because of their low corrosion resistance in the anode environment (Fig. 10), a protective coating (e.g., nickel) is required there. To eliminate the need of this protective coating, single-alloy bipolar current collector materials that perform acceptably in both environments need to be developed.

5.1. Corrosion mechanisms

Although primary efforts so far have been focused on material screening, some understanding of corrosion mechanisms has been achieved, by analyzing steady-state, thermogravimetric and potential sweep results, supported by thermodynamic calculation [11,39–49].

In the reducing anode environment, an unprotected austenitic stainless-steel surface forms a thick bi-layered oxide scale (Figs. 10 and 11). The inner layer is rich in iron and chromium and the compact chromia layer appears absent [39,44]. Nickel-rich metallic islands are also present in the inner oxide scale. The outer scale consists primarily of lithiated, large-crystalline iron oxide. Chromium also depletes at the metal–oxide interface. Selective etching revealed carburization of the substrate metal. A comprehensive thermodynamic analysis predicted LiFeO₂ outer scale and LiCrO₂ inner scale [46], although the corrosion rate cannot be easily estimated. Deep-melt potential sweep results [48,49] showed active/passive characteristics, with the active region near the anode potentials (–0.8 to –1.0 V relative to a 33O₂/67CO₂ reference electrode) and the somewhat passive region near the

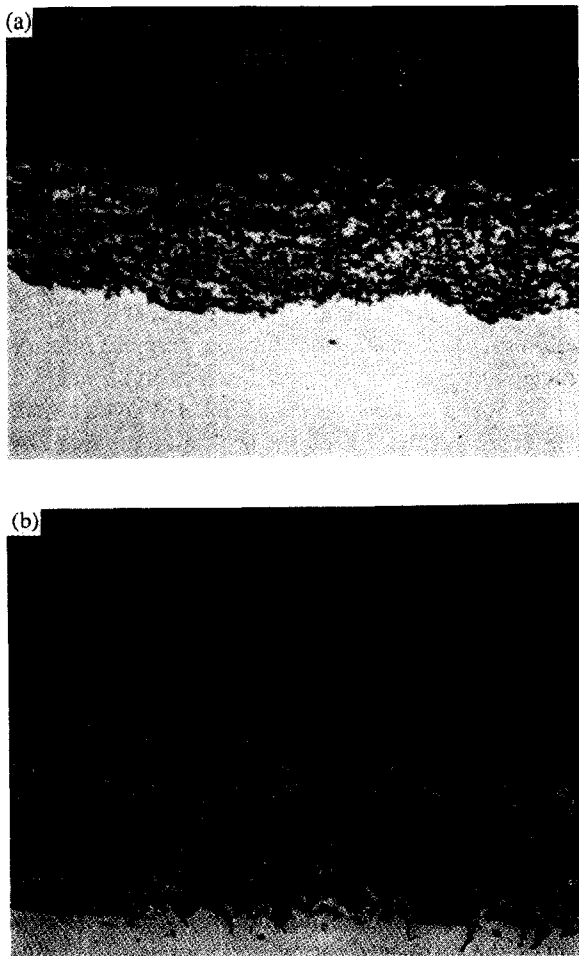


Fig. 10. Hot corrosion of stainless steel (a) 310S and (b) 316L in anode environment (650 °C, 1000 h): fast corrosion in anode environment ($\times 270$).

cathode potential. No detailed mechanism has been elucidated to date to clearly explain this high corrosion rate near the anode potential. It appears that the Fe–Cr inner scale does not sufficiently reduce substrate iron diffusion to the oxide

surface. The combined effects of iron fluxing and carburization may also contribute to the high anode-side corrosion rate. A better mechanistic understanding will be useful to assist alloy design to eliminate the presently required nickel coating. Although the high-nickel nickel-base alloys such as Inconel 600 have demonstrated better corrosion resistance than stainless steels, significant internal oxidation of chromium to LiCrO_2 still occurred [42]. Recently, a high Ni–Cr alloy with small amounts of aluminum and yttrium (40Ni–30Cr–1Al–Y) has been shown to have good corrosion resistance in both anode and cathode environments [16,50]. Long-term cell/stack testing is needed to qualify this alloy.

In the oxidizing cathode environment, hot corrosion phenomena appear to be reasonably understood [40,47]. The oxide scale formed at 310S and 316L has a multi-layered structure (LiFeO_2 outer, chromium-rich inner and sometimes intermediate scales), as shown in Fig. 12. The outer scale formed at the cathode contact surface contains a large amount of nickel (> 20 mol%), originating from the NiO cathode, and a small amount of manganese (< 3 mol%), from the stainless-steel substrate. The chromium content in the outer scale is generally very low (< 2 mol%). The chromium-rich inner scale also contains significant amounts of iron and nickel; Cr_2O_3 , FeCr_2O_4 and NiCr_2O_4 have been identified [51]. A thin Cr_2O_3 layer is present at the metal-scale interface and appears more compact at 310S (containing 25% Cr) than at 316L (containing 18% Cr) [52]. A comprehensive thermodynamic analysis [46] predicted LiFe_5O_8 – LiCrO_2 – Cr_2O_3 scale for 310S and LiFeO_2 – LiFe_5O_8 – Fe_xO_y – FeCr_2O_4 – Cr_2O_3 scale for 316L, in fairly good agreement with X-ray diffraction results. The deep-melt potential sweep experiments [48] showed passivation characteristics, although the corrosion current is still not low, explainable by the continuous fluxing of chromium to soluble chromate. Enhancement of the protectiveness of the outer lithiated iron oxide scale to reduce chromium fluxing has been shown to improve 316L corrosion resistance [53].

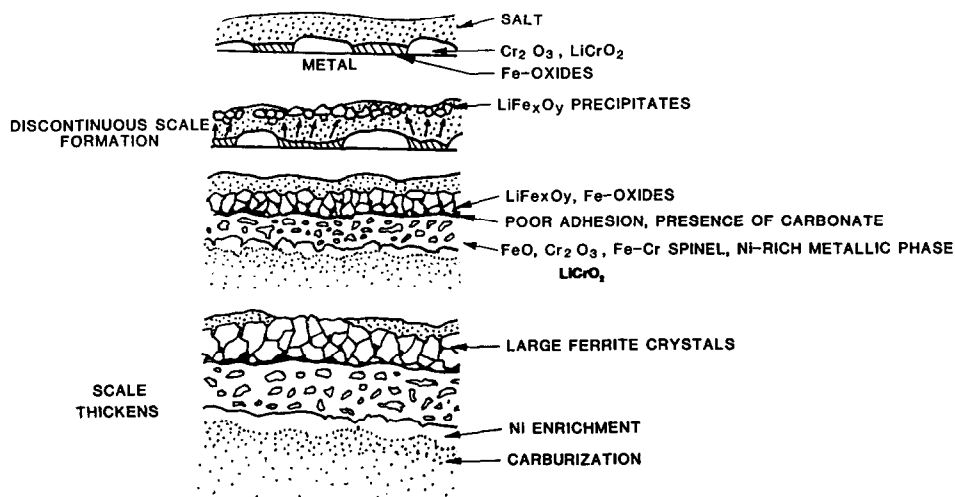


Fig. 11. Formation of oxide scale at austenitic stainless steel in anode environment: oxide scale is thick and unprotective.

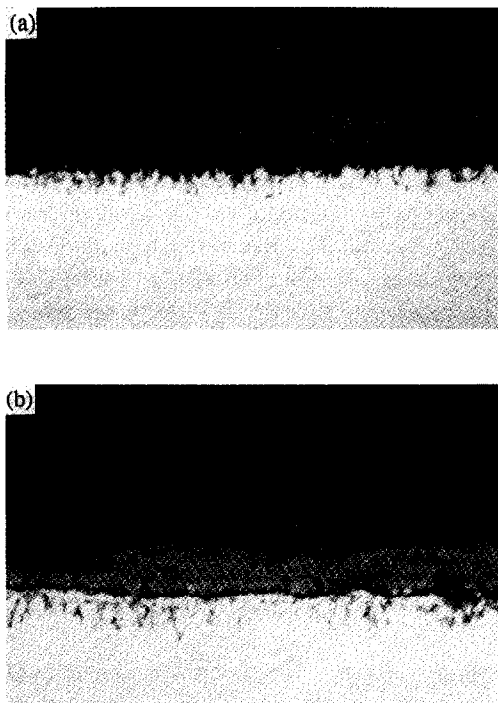


Fig. 12. Hot corrosion of stainless steel (a) 310S and (b) 316L in cathode environment (650 °C, 1000 h): 310S more corrosion resistant than 316L ($\times 550$).

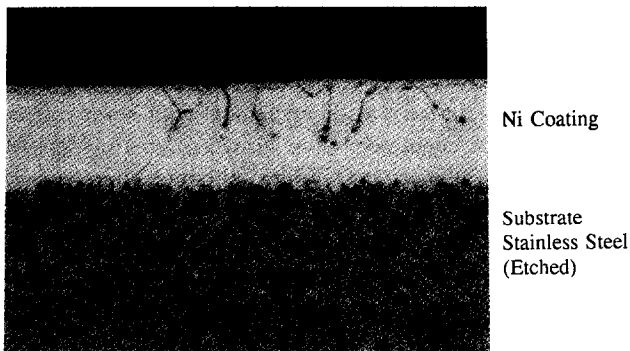


Fig. 13. Nickel clad coating after 10 000 h: stable nickel coating provides sufficient protection ($\times 130$).

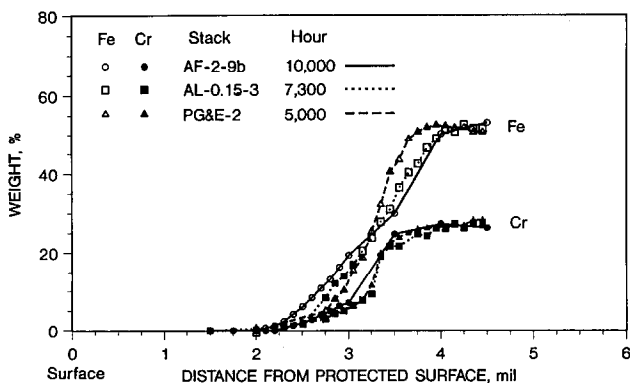


Fig. 14. Nickel-substrate interdiffusion after 10 000 h: 50 μm nickel coating appears adequate for 40 000 h use.

5.2. Endurance of anode-side materials

Surface protection of stainless steels by thermodynamically stable nickel coating has generally been adopted by fuel cell developers. Nickel can be applied by either plating or cladding. Electroless nickel coating has excellent thickness uniformity but is not used because of the high plating cost as well as the low stability caused by the high phosphorus content in Ni–P coating [11]. Electrolytic nickel plating (e.g., sulfamate bath) produces a very pure nickel coating but has nonuniform thickness distribution on current collectors of corrugated shapes. Furthermore, the electrolytic nickel structure may not be as dense as the nickel clad layer, which has a very dense structure. With the protection provided by the nickel clad coating, the anode-side bipolar plate has shown virtually no corrosion attack for up to 10 000 h operation (Fig. 13). Consequently, no significant ohmic loss due to anode-side contact interfacial resistance was observed. Although a small amount of chromium-rich oxide forms at the grain boundaries of the nickel clad layer (diffused into the coating from the substrate stainless steel), no deleterious effect on the corrosion protection is observed. The coating has also shown excellent thermal cycleability (up to six cycles in a stack test). The interdiffusion profiles in the nickel clad coating during the 5000–10 000 h testing is shown in Fig. 14. The diffusion of iron and chromium into the coating appears tolerable. Based on this result, a nickel thickness of 50 μm may be adequate for 40 000 h use.

Because of the thickness nonuniformity of the electrolytic nickel on the corrugated current collector, to plate sufficient nickel to the recessed area will require some areas excessively plated, resulting in high plating cost. Therefore, methods to coat nickel uniformly at low cost are desirable. The most desirable solution is to eliminate the need of nickel coating, if a single-alloy bipolar current collector material is developed. Significant cost benefit can be realized.

Copper coating, although is more cost effective than nickel, is not compatible with the state-of-the-art nickel anode. Fast Ni–Cu interdiffusion has been observed in cell tests, resulting in densification of the Ni–Al anode and pore formation in the copper coating. Therefore, the use of copper coating requires a copper-base anode, which is not yet available due to its low creep strength.

5.3. Endurance of cathode-side materials

Metallographic analysis of the 316L cathode-side current collectors has shown that the corrosion resistance of 316L appears acceptable for 40 000 h use (Fig. 15). Oxide scale formed at 316L after long-term stack testing appears still compact (Fig. 16). Electrolyte loss associated with the corrosion was reviewed elsewhere [52]. The 310S, due to its higher chromium content, has shown better corrosion resistance than 316L. However, more electrolyte loss has been observed for 310S.

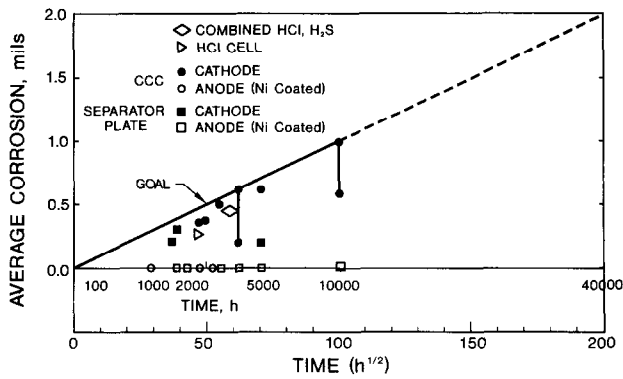


Fig. 15. Corrosion of bipolar current collector: 316L appears adequate for 40 000 h use in cathode environment.

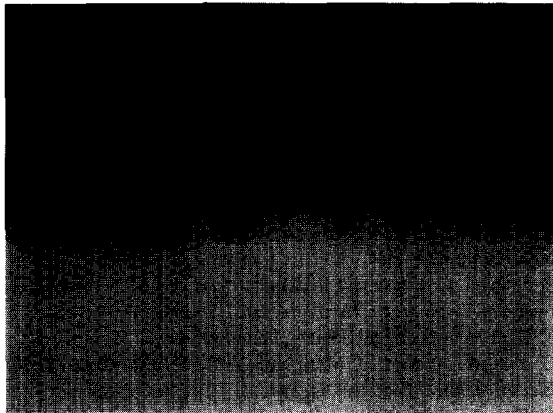


Fig. 16. Oxide scale formed at 316L after 7000 h stack testing: oxide scale appears still compact ($\times 290$).



Fig. 17. Aluminized coating after 20 000 h testing: coating provides adequate protection ($\times 240$).

Another selection consideration is ohmic resistance of the oxide scale formed at the contact area. The presently used 316L is expected to contribute about 10 mV oxide ohmic loss at beginning-of-life (BOL) and 100 mV after 40 000 h [52]. Surface modification to improve oxide scale conductivity may be possible [53].

5.4. Wet-seal materials

The wet-seal simultaneously experiences reducing and oxidizing environments; chromia-forming alloys experi-

enced high corrosion. Only alumina-forming alloys are acceptable in such an environment [54]. Because it is difficult and expensive to manufacture a bipolar current collector incorporating a bulk aluminum-containing alloy to the wet-seal area, aluminized coating has generally been selected [11,55,56].

Aluminizing methods evaluated so far include painting, thermal spraying and vacuum deposition (followed by diffusion heat treatment) and pack cementation. Pack cementation generally produces too deep a diffusion layer and may cause warpage to large-size bipolar plates. The resultant diffused coating on stainless-steel surface generally consists of a $MAI-M_3Al$ structure (M = iron, nickel, plus 5–15 mol% chromium). A hard chromium-rich phase and an inner layer with secondary phase inclusions (possibly carbide and σ phases) are also present. The coating has been shown to provide sufficient protection for the substrate stainless steels during a 20 000 h testing (Fig. 16). Concentration of aluminum in the coating is still very high (30 mol%) after 20 000 h (Fig. 17). Based on these results, it may be projected that the stability of aluminized coating is adequate.

The major development drive now is to investigate various aluminizing processes for cost reduction. Aluminizing methods without the need of expensive diffusion heat-treatment step will be very desirable. Thermal spraying of aluminum-containing alloy powders such as $FeCrAlY$, MAI or M_3Al (M = nickel, iron) may be an alternate approach. However, the porous structure of the coating produced so far needs to be improved to prevent carbonate attack of the substrate.

6. Conclusions

Based on the long-term stack testing results, the present anode, cathode matrix and bipolar current collector materials have acceptable performance and endurance for large-scale demonstration. However, cost reduction is desired to assure rapid commercialization. Many improvement opportunities have been identified (summarized in Table 1) that may extend life well beyond the present 40 000 h and achieve further cost reduction.

References

- [1] L. Blomen and M. Mugerwa (eds.), *Fuel Cell Systems*, Plenum, New York, 1993.
- [2] J. Appleby and F. Folkes, *Fuel Cell Handbook*, Van Nostrand Reinhold, New York, 1990.
- [3] B. Baker, C. Bentley and D. Glenn, *Fuel Cells '94 Contractors Review Meet., Morgantown, WV, USA, 17-18 Aug. 1994*, p. 123.
- [4] C. Yuh and J.R. Selman, *J. Electrochem. Soc.*, 131 (1984) 2062.
- [5] C. Yuh and J.R. Selman, *J. Electrochem. Soc.*, 138 (1991) 3642.
- [6] A. Pigcaud, H. Maru, L. Paetsch, J. Doyon and R. Bernard, *Proc. Symp. Porous Electrodes: Theory and Practice, Detroit, MI, USA, Oct. 1992*, Proc. Vol. 84-8, The Electrochemical Society, Pennington, NJ, USA, p. 234.
- [7] C. Iacovangelo, *J. Electrochem. Soc.*, 133 (1986) 2410.

- [8] H. Urushibata and T. Murahashi, *Proc. Int. Fuel Cell Conf., Makuhari, Japan, 1992*, Paper No. III-E-2.
- [9] C. Iacovangelo, *J. Electrochem. Soc.*, 133 (1986) 1359.
- [10] L. Paetsch, J. Doyon, R. Chamberlin and C. Yuh, *Ext. Abstr., Fall Meet. Electrochemical Society, Honolulu, HI, USA, May 1987*.
- [11] Energy Research Corporation, Final Rep. US DOE under Contract No. DE-AC01-76ET11304 (1987).
- [12] G. Kucera, K. Myles, A. Brown, M. Roche, D. Chu and E. Indacochea, *Proc. 4th Annual Fuel Cells Contractors Review Meet., Morgantown, WV, USA, 31 July 1992*.
- [13] K. Myles, M. Krumpelt, G. Kucera, M. Roche and E. Indacochea, *Proc. Joint Contractors Meet: Advanced Turbine Systems, Fuel Cells and Coal-Fired Heat Engines Conf., Morgantown, WV, USA, 3–5 Aug. 1993*, p. 386.
- [14] S.H. Lu, *Proc. 2nd Symp. Molten Carbonate Fuel Cell Technology, Seattle, WA, USA, Oct. 1990*, Proc. Vol. 90-16, The Electrochemical Society, NJ, USA, p. 251.
- [15] K. Hoshino and T. Kohno, *Proc. Int. Fuel Cell Conf., Makuhari, Japan, 1992*, Paper No. III-B-4.
- [16] T. Yoshi, K. Hoshino, N. Ariga, M. Yamamoto and Y. Horii, *Ext. Abstr., 1994 Fuel Cell Seminar, San Diego, CA, USA, Nov./Dec. 1994*, National Fuel Cell Coordinating Group, Washington DC, 1994, p. 140.
- [17] R. Reed-Hill, *Physical Metallurgy Principles*, Van Nostrand Reinhold, New York, 1973.
- [18] C. Yuh, *Proc. Symp. High-Temperature Electrode Materials and Characterization, Washington, DC, USA, May 1991*, Proc. Vol. 91-6, The Electrochemical Society, Pennington, NJ, USA, p. 257.
- [19] R. Pierce, J. Smith and R. Poepfel, *Proc. Symp. Molten Carbonate Fuel Cell Technology, Montreal, Canada, May 1982*, Proc. Vol. 82-13, The Electrochemical Society, Pennington, NJ, USA, p. 147.
- [20] I. Uchida, K. Yamada, T. Nishina and J.R. Selman, *Proc. Symp. High Temperature Electrode Materials and Characterization, Washington, DC, USA, May 1991*, Proc. Vol. 91-6, The Electrochemical Society, Pennington, NJ, USA, p. 239.
- [21] C. Yuh and J.R. Selman, *J. Electrochem. Soc.*, 138 (1991) 3649.
- [22] J.R. Selman and G. Lee, *Proc. 3rd Int. Symp. Carbonate Fuel Cell Technology, Honolulu, HI, USA, May 1993*, Proc. Vol. 93-3, The Electrochemical Society, Pennington, NJ, USA, p. 309.
- [23] C. Yuh, Topical Rep. US DOE under Contract No. DE-AC21-90MC27168 (May 1991).
- [24] W. Vogel, L. Bregoli, H. Kunz and S. Smith, *Proc. Symp. Molten Carbonate Fuel Cell Technology, Montreal, Canada, May 1982*, Proc. Vol. 82-13, The Electrochemical Society, Pennington, NJ, USA, p. 443.
- [25] C. Baumgartner, *J. Ceram. Soc.*, 69 (1986) 162.
- [26] International Fuel Cells Corporation, Final Rep. US DOE under Contract No. DE-AC21-79ET15440 (Feb. 1988).
- [27] D. Shores, J.R. Selman, S. Israni and E. Ong, *Proc. 2nd Symp. Molten Carbonate Fuel Cell Technology, Washington, DC, USA, May 1990*, Proc. Vol. 90-16, The Electrochemical Society, Pennington, NJ, USA, p. 290.
- [28] H. Kasai and A. Suzuki, *Proc. 3rd Int. Symp. Carbonate Fuel Cell Technology, Honolulu, HI, USA, May 1993*, Proc. Vol. 93-3, The Electrochemical Society, Pennington, NJ, USA, p. 240.
- [29] S. Yoshioka and H. Urushibata, *Ext. Abstr., 186th Electrochemical Society Meeting, Miami, FL, USA, Oct. 1994*, Abstr. Vol. 94-2, p. 938.
- [30] H. Kunz and L. Bregoli, *Proc. 2nd Symp. Carbonate Fuel Cell Technology, Seattle, WA, USA, Oct. 1990*, Proc. Vol. 90-16, The Electrochemical Society, Pennington, NJ, USA, p. 157.
- [31] H. Kunz and J. Pandolfo, *J. Electrochem. Soc.*, 139 (1992) 1549.
- [32] L. Plomp, J. Veldhuis, E. Sitters, F. Van Berkel and S. Van der Molen, *Proc. International Fuel Cell Conf., Makuhari, Japan, 1992*, Paper III-B-1.
- [33] J. Smith, G. Kucera and A. Brown, *Proc. 2nd Symp. Molten Carbonate Fuel Cell Technology, Seattle, WA, USA, Oct. 1990*, Proc. Vol. 90-16, The Electrochemical Society, Pennington, NJ, USA, p. 225.
- [34] L. Plomp, E. Sitters, J. Veldhuis, R. Makkus and S. Van der Molen, *Proc. 3rd Int. Symp. Carbonate Fuel Cell Technology, Honolulu, HI, USA, May 1993*, Proc. Vol. 93-3, The Electrochemical Society, Pennington, NJ, USA, p. 171.
- [35] B. Bergman, C. Lagergren and A. Lundblad, *Proc. 3rd Int. Symp. Carbonate Fuel Cell Technology, Honolulu, HI, USA, May 1993*, Proc. Vol. 93-3, The Electrochemical Society, Pennington, NJ, USA, p. 342.
- [36] L. Paetsch, J. Doyon and M. Farooque, *Proc. 3rd Int. Symp. Carbonate Fuel Cell Technology, Honolulu, HI, USA, May 1993*, Proc. Vol. 93-3, The Electrochemical Society, Pennington, NJ, USA, p. 89.
- [37] Energy Research Corporation, Final Rep. US DOE under Contract No. DE-AC21-90MC23274 (1990).
- [38] K. Faber and A. Evans, *Acta Metall.*, 31 (1983) 565.
- [39] Energy Research Corporation, Final Rep. US DOE, under Contract No. DE-AC21-84MC21186 (1986).
- [40] D. Shores and P. Singh, *Proc. Symp. Molten Carbonate Fuel Cell Technology, Montreal, Canada, May 1982*, Proc. Vol. 82-13, The Electrochemical Society, Pennington, NJ, USA, p. 271.
- [41] IIT Research Institute, Final Rep. US DOE under Contract No. DE-AC21-86MC23265 (1990).
- [42] P. Singh and H. Maru, *Corrosion* 85, Boston, MA, USA, Mar. 1985, NACE, Paper No. 344.
- [43] T. Nishina, K. Yuasa and I. Uchida, *Proc. 3rd Int. Symp. Carbonate Fuel Cell Technology, Honolulu, HI, USA, May 1993*, Proc. Vol. 93-3, The Electrochemical Society, Pennington, NJ, USA, p. 264.
- [44] C. Yuh, A. Pigeaud, H. Maru and G. Meier, *Ext. Abstr., Fall Meet. Electrochemical Society, Chicago, IL, USA, Oct. 1988*.
- [45] D. Shores and M. Pischke, *Proc. 3rd Int. Symp. Carbonate Fuel Cell Technology, Honolulu, HI, USA, May 1993*, Proc. Vol. 93-3, The Electrochemical Society, Pennington, NJ, USA, p. 214.
- [46] H. Yokokawa, N. Sakai, T. Kawada, M. Dokiya and K. Ota, *J. Electrochem. Soc.*, 140 (1993) 3565.
- [47] C. Yuh, R. Johnsen, M. Farooque and H. Maru, *Proc. 3rd Int. Symp. Carbonate Fuel Cell Technology, Honolulu, HI, USA, May 1993*, Proc. Vol. 93-3, The Electrochemical Society, Pennington, NJ, USA, p. 158.
- [48] K. Nakagawa, T. Isozaki and S. Kihara, *Boshoku Gijutsu*, 36 (1987) 438.
- [49] K. Nakagawa, S. Kihara and S. Ito, *Boshoku Gijutsu*, 37 (1988) 478.
- [50] T. Shimada, Y. Kuriki, N. Yamanouchi and M. Tamura, *Proc. 1990 Fuel Cell Seminar, Tucson, AZ, USA, 25–28 Nov. 1990*, p. 171.
- [51] Y. Fujita, H. Urushibata, K. Sato and T. Murahashi, *Proc. Fall Meet. Electrochemical Society, Japan, 1989*, 2E04, p. 115.
- [52] C. Yuh, M. Farooque and R. Johnsen, *Proc. 4th Annual Fuel Cells Contractors, Review Meet., Morgantown, WV, USA, 14–15 July 1992*, p. 53.
- [53] Energy Research Corporation, Final Rep. US DOE under Contract No. DE-AC01-89ER80849 (1990).
- [54] R. Donado, L., Marianowski, H. Maru and J.R. Selman, *J. Electrochem. Soc.*, 131 (1984) 2535.
- [55] C. Yuh, P. Singh, L. Paetsch and H. Maru, *Corrosion* 87, San Francisco, CA, USA, Mar. 1987, Paper No. 276.
- [56] M. Yamamoto and Y. Kato, *Ext. Abstr., 1994 Fuel Cell Seminar, San Diego, CA, USA, Nov./Dec. 1994*, National Fuel Cell Coordinating Group, Washington DC, USA, p. 144.