

An analysis of endurance issues for MCFC

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Abstract

For high temperature fuel cells in combined heat and power applications, it is generally assumed that a stack lifetime of at least 40,000 h is required in order to achieve cost-of-electricity targets. From existing experience, it is known that lifetime limiting issues for molten carbonate fuel cell (MCFC) systems are mainly materials issues of the stack. An overview is given of the most critical endurance issues of the MCFC stack. In addition, it is argued that under specific operating conditions of the system, the stack is expected to have lifetimes over 40,000 h with the use of state-of-the-art materials, based on model calculations. Clearly, the estimated endurance data need to be verified by long-term stack and system tests. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: MCFC stack; MCFC system; Endurance; Lifetime; Cost-of-electricity; 40,000 h

1. Introduction

The commercial introduction of the Molten Carbonate Fuel Cell (MCFC) system for co-generation or electricity production can only be successful if the technology can compete with existing conventional technologies and other technologies under development. Worldwide, the MCFC technology is entering the 0.1–2 MW demonstration phase for verification of initial performance and efficiency, and for obtaining operating experience [1–5]. For economic reasons, the MCFC stack, which converts the fuel into electricity and heat, should have a long lifetime. Improvement of the endurance of the MCFC stack and its components is an important issue in the worldwide R&D on MCFC [6].

An overview of endurance aspects for MCFC fuel cell stacks is presented. The several aspects of endurance of MCFC are discussed in detail. Examples, data and illustrations have largely been taken from the development programme of the Advanced Direct Internal Reforming (DIR)-MCFC consortium for reasons of availability of the data. Within the consortium, a development programme has been carried out on second generation DIR-MCFC systems and stacks. The consortium consists of Brandstof-

cel Nederland BCN (Stork, Schelde and ECN), BG Technology, Gaz de France and Sydkraft.

2. Lifetime requirement for MCFC stacks

The commercial introduction of the MCFC systems into the market depends on economic factors like existing prices of gas and electricity, governmental regulations and the degree of liberalisation of the energy market. These factors vary strongly for each country and with time. For the present Dutch situation, as was concluded in the DIR-MCFC programme development consortium, the main conventional competitors in the CHP-market are the gas engine and the gas turbine. The lifetime requirement of the MCFC stack can be estimated by calculating the Cost of Electricity (CoE) of MCFC system as a function of stack lifetime and comparing it with the CoE of the conventional technologies (Fig. 1). The main assumptions for calculating economic viability are:

- Investment cost stack US\$500/kW_e
- Investment cost Balance of Plant (BOP) US\$500/kW_e
- Lifetime BOP is 15 years
- Electrical efficiency of the system 50%
- Thermal efficiency of the system 30%
- Maintenance cost US\$0.005/kW h_e
- Natural gas cost US\$0.018/kW h_{th}
- CoE for conventional technology US\$0.05/kW h_e

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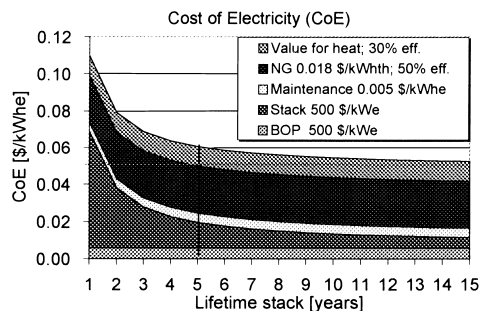


Fig. 1. CoE vs. lifetime of the MCFC stack.

Accordingly, the minimum required lifetime for the MCFC stack is 5 years, provided that the system is used for co-generation, i.e., the heat produced also has an economic value in the assumptions made.

3. Lifetime limiting issues for MCFC

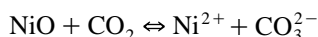
The question arises as to what the lifetime of the MCFC stack will be, after solving the technological problems in the design and operation of commercial scale systems. Known lifetime limiting phenomena are:

1. Dissolution of NiO cathode
2. Electrolyte losses
3. Corrosion of separator plate
4. Electrolyte retention capacity
5. Catalyst deactivation
6. Matrix cracking
7. High temperature creep of porous components
8. Contaminants.

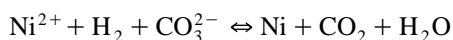
These phenomena are addressed in Sections 3.1, 3.2, 3.3, 3.4, 3.5, 3.6, 3.7 and 3.8.

3.1. Dissolution of NiO cathode

The cathode widely used in the MCFC stack is porous NiO. The material is not stable in the MCFC, but it dissolves due to the reaction:



The Ni^{2+} ions move into the matrix towards the anode. At the same time, hydrogen diffuses into the matrix from the anode side and at a certain distance away from the cathode the Ni^{2+} ions are reduced by the reaction:



The metallic nickel precipitates in the pores of the matrix (Fig. 2). This will eventually lead to short-circuiting across the matrix, resulting in a reduced performance of the cell. The process primarily depends on $p\text{CO}_{2,\text{Cathode}}$, $p\text{H}_{2,\text{Anode}}$, matrix thickness d_M , and the electrolyte composition. Solutions proposed and investigated are: (1) the addition of rare earth additives to either the NiO cathode

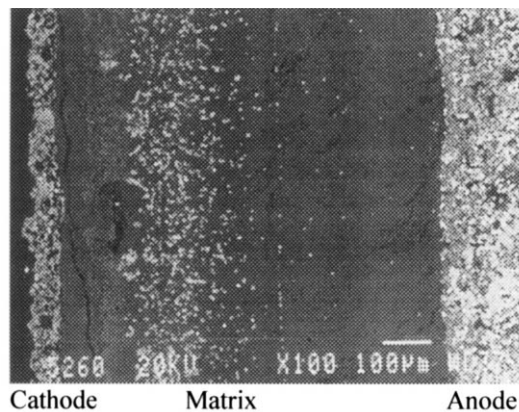


Fig. 2. Nickel precipitation in matrix after 6000 h stack experiment.

itself or to the electrolyte, (2) a NiO cathode coated with LiCoO_2 and (3) a pure LiCoO_2 cathode [7–9].

3.2. Electrolyte losses

In the MCFC, stack loss of electrolyte occurs due to reaction of the electrolyte with the stack components resulting in lithiation of electrodes and the Al_2O_3 fibres in the matrix, and corrosion of hardware. Also, the stack hardware is wetted by electrolyte. These processes cause loss of electrolyte, mainly during the first 1000 h of operation. Continuous loss of electrolyte, predominantly K_2CO_3 , is caused by evaporation of electrolyte from the stack. This process primarily depends on $p\text{H}_2\text{O}$, $p\text{CO}_2$, volume gas flow, temperature and the electrolyte composition [10,11].

An example of the electrolyte inventory of a stack after 6000 h of operation and loss mechanisms responsible is shown by Fig. 3.

3.3. Corrosion of separator plate

For the separator plate, several designs are applied worldwide. A major division can be made between internally manifolded designs and externally manifolded designs. In the former, the gas supply system is integrated into the separator plate. Sealing of the cell is achieved by a circumferential zone in which the matrix tile is extended;

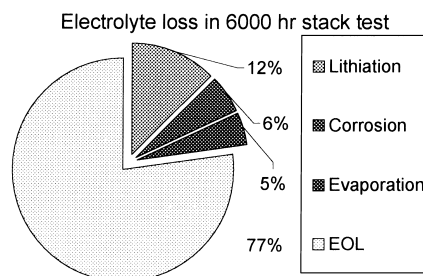


Fig. 3. Electrolyte losses after 6000 h of operation in a 10-cell stack experiment with Li/K electrolyte.

the wet-seal area. Corrosion of the separator plate can lead to short-circuiting if conductive corrosion products precipitate at the wet-seal area, and can lead to the direct reaction of fuel and oxidant if the mid-plate of the separator plate is perforated. The following measures have been used in order to avoid corrosion.

- A non-conducting coating is implemented at the wet-seal; aluminisation of the base material seems to be sufficiently protection. Also, Al–Ni plated material is reported to be sufficiently protecting [12].

- For the oxidant side of the mid-plate, the base material of the plate to which the gas composition of the plate is exposed and the degree of electrolyte wetting determine the lifetime. Most developers expect either AISI 316 or AISI 310 to have adequate corrosion resistance.

- At the fuel side, a nickel layer is usually applied. However, it is found that internal oxidation of this nickel layer occurs (Fig. 4). Eventually, this mechanism causes complete breakdown of the protective properties and subsequent rapid attack of the base material occurs. The rate of internal oxidation depends on the H_2/H_2O ratio, the temperature and the coating thickness and this may be responsible for the fact that developers disagree on the lifetime of a nickel coating.

3.4. Electrolyte retention capacity

The state-of-the-art matrix consists of γ -LiAlO₂ that converts into the higher density γ -LiAlO₂ phase during operation of the stack. This process is accompanied by particle growth and pore size increase of the matrix [13,14]. This can lead to a loss of capillary retention for electrolyte in the matrix, which causes redistribution of electrolyte and will finally result in the cross-over of gas. An example of pore size increase after 6000 h of operation in a stack experiment is shown in Fig. 5. In Refs. [13,14], as a solution for this problem, it has been suggested that the matrix be manufactured from γ -LiAlO₂ initially.

3.5. Catalyst deactivation

In case of the internal reforming (IR) MCFC, the reforming catalyst is placed in the anode compartment.

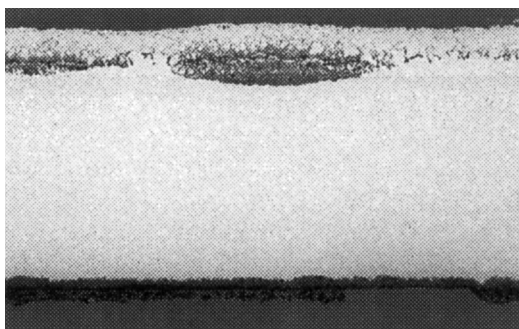


Fig. 4. Internal oxidation of the AISI 316 separator mid-plate with 50 μ m Ni-clad layer after 6000 h stack experiment.

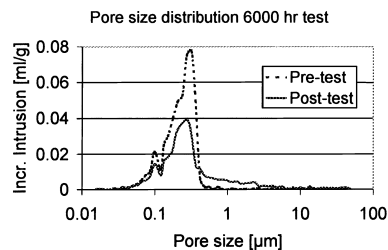


Fig. 5. Pore size distribution of matrix after 6000 h stack experiment.

Deactivation of the catalyst occurs by sintering of the carrier material or of the nickel crystallites, the most commonly used reforming catalyst material. Secondly, transport of electrolyte by migration or by evaporation and subsequent deposition can fill the pores of the carrier and deactivate the catalyst [15,16]. Calculations for the sensitivity of performance and for methane conversion on catalyst activity suggest that some deactivation is permissible (Fig. 6).

3.6. Matrix cracking

The matrix should be gas-tight for separation of the oxidant and fuel gases. If cracks occur in the matrix, oxidant and fuel gas will react (cross-over) and local overheating of the cell occurs. Additionally, reduction of the cathode or oxidation of the anode causes performance loss. Thermal cycling of the stack is considered the major cause for matrix cracking. Apart from thermal cycling during conditioning of the stack in the factory and during start-up at the plant, thermal cycling of MCFC stacks occurs for reasons of maintenance or failures in operation of the system. Results for cross-over induced by thermal cycling scatter strongly (Fig. 7) and data on thermal cycling have not been systematically presented until now. Because of the large and immediate performance loss associated with cross-over, resistance to thermal cycling must be considered as a major critical issues for stack lifetime.

3.7. High temperature creep of porous components

Sintering and mechanical creep of components, and dissolution of the cathode cause thinning of porous compo-

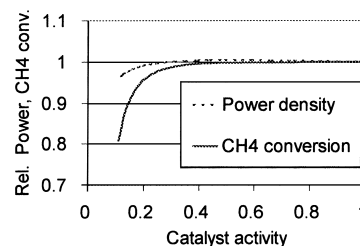


Fig. 6. CH₄-conversion and relative power density as function of the catalyst activity.

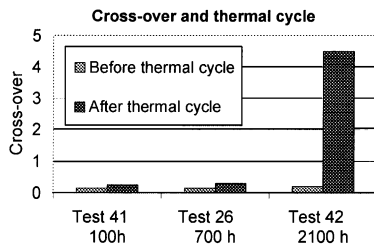


Fig. 7. Gas cross-over before and after a thermal cycle for three stack experiments as determined with a volume flow balance.

nents [17,18]. As a consequence, loss of electrical contact between the components making up the stack will probably occur. In the case of internal manifolding stacks, flexible wet-seal areas between the separator plates avoids this problem. Flexibility in the design facilitates the preservation of electrical contact between the cells and separator plates. An example of the shrinkage in an internally manifolded stack measured in situ after 6000 h operating time, and the post-test determined reduction in component thickness is shown in Fig. 8.

3.8. Contaminants

Contaminants in the fuel, such as sulphur or chlorine compounds, interfere with electrode processes. Until now, it has been found difficult to determine the maximum allowable contamination level in experiments [19]. However, it is to be expected that appropriate gas clean-up will be necessary in field tests to keep the level of contaminants sufficiently low.

4. System aspects

The lifetime of the components in the stack not only depends on the materials used, as discussed above, but is also dependant on the operating conditions in the stack, which are directly related to the system design. Important parameters for lifetime, determined by the system are:

- Atmospheric or pressurised operation;

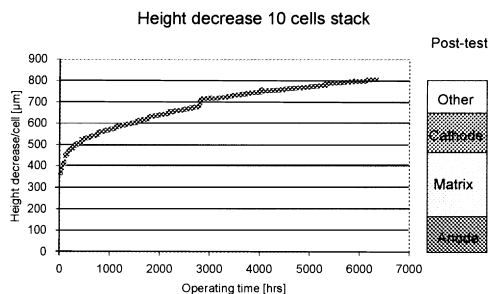


Fig. 8. Shrinkage of stack and corresponding component thickness reduction from post-test analysis.

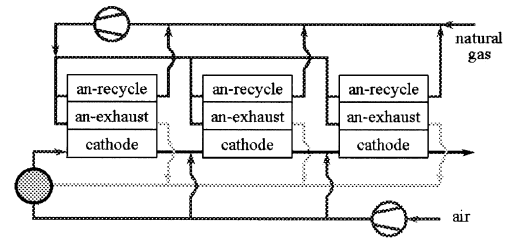


Fig. 9. The “Advanced DIR-MCFC” system design comprising three stacks.

- Internal or external reforming;
- Gas recycling: none/fuel/oxidant;
- Water: injection/removal/none; and
- Operating temperature.

Often, a balance has to be found between these parameters. For example, pressure increase has a positive lifetime effect on electrolyte loss, but a negative lifetime effect on cathode dissolution. Because of the large differences in MCFC systems under development, general lifetime estimations for MCFC systems cannot be given.

In Section 5, a system design will be described which resulted from the “Advanced DIR-MCFC development” programme [20]. The aim of this programme was the development of a simple, low cost system with improved lifetime of the stack. The selected system, i.e., the so-called “Smarter design”, is characterised (Fig. 9) by series connection of the stacks and operation at ambient pressure. Furthermore (cf. Fig. 9), the system is operated by internal reforming, fuel gas recycling, no water injection nor removal and is designed for as low as possible operating temperatures. For the stack, an internally manifolded, co-flow configuration was developed which can be operated within the system interface conditions. BG Technology developed the IR-catalyst. Full size (1 m²) stack specifications were developed that enable large differential pressures across the stack and a stack service life $\geq 25,000$ h. Validation of the stack technology was carried out on 0.1 m² active components and the results were compared with models for stack and active components. On the basis of

Table 1

Lifetime estimation for components in “Advanced DIR-MCFC development” stack

Component	State-of-art	Endurance (h)	Alternatives
Anode	Ni–Cr	40,000	
Cathode	NiO	40,000	
Matrix	γ -LiAlO ₂ + Al ₂ O ₃	40,000 (no TC)	
Electrolyte	Li/Na/K 60/20/20	25,000–40,000	Li/Na
Catalyst	BG technology	6000–40,000	IIR, ER
Separator	AISI 310 S	40,000	
Coating anode	Ni-clad layer	10,000–15,000	Coating type
Wet-seal	Aluminised	40,000	

this philosophy, the lifetime estimation for the components in the Smarter system is given in Section 5.

5. Lifetime estimation

Table 1 shows the selected state-of-the-art components to be implemented in an ‘‘Advanced DIR-MCFC development’’ stack and the lifetime estimations. On the basis of extrapolations from models, 5 years lifetime is predicted for the anode, cathode, matrix (without thermal cycling), separator base material and the wet-seal coating. However, this still has to be verified in long-term stack experiments at realistic system conditions. With the electrolyte composition selected, 5 years lifetime, based on evaporation models, is attainable. Out-of-cell tests, including electrolyte deposition, predict a long lifetime for the catalyst, but this is still to be proven in stack experiments. For the fuel side of the separator plate, a new coating with sufficient lifetime has been developed, it has to be integrated with the separator plate fabrication.

6. Conclusions

For the endurance of MCFC stacks it is concluded that:

- 5 years stack lifetime is required on the basis of an economic analysis of cost-of-electricity.
- Lifetime limitation is mainly a materials issue of the stack at the moment.
- Thermal cycling of the stack is considered to be most critical, though limited attention is given to the subject worldwide.
- (D)IR catalyst endurance has to be proven in stacks.
- Optimum system designs, e.g., ‘‘Smarter’’, promise 5 years of stack service life.
- Long-term stack tests under system conditions are further required for validation of endurance models predicting stack service lifetime.

Acknowledgements

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