Short communication

High temperature corrosion of metallic materials in molten carbonate fuel cells environment ☆

G. Durante [a, *], S. Vegni [a], P. Capobianco [a], F. Golgovici [b]

[a] *Ansaldo Fuel Cells S.p.a., Genoa, Italy*
[b] *Polytechnic University of Bucharest, Bucharest, Romania*

Abstract

Molten carbonate fuel cells (MCFCs) are electrochemical devices that convert energy of a chemical reaction into electricity without any kind of combustion. So, MCFCs are promising for their high efficiency and their low environmental pollution.

A limiting aspect for reaching the goal of 40,000 h of life-time is the corrosion of metallic parts of MCFC, especially for current collectors and separator plates.

Generally, this corrosion leads to metal loss and to an important increase of the electrical resistance due to the formation of resistive oxides.

One of the most critic components in a MCFC is the anodic side metallic components. More used choice for these components is actually a sheet of AISI310S cladded at both sides by a Ni layer.

The analysis of the behaviour of this material after different steps of corrosion in a typical molten carbonate fuel cell environment could be important to understand some phenomena that cause the damage of the anodic current collector.
© 2005 Elsevier B.V. All rights reserved.

Keywords: MCFC; High temperature corrosion; Electrical conductivity

1. Introduction

The molten carbonate fuel cells (MCFCs) can be considered as a new and alternative power source, promising for its low environmental emission and for its high efficiency.

They can convert into electricity the chemical energy of a reaction with no intermediate conversion of heat into mechanical energy [1].

In Fig. 1, the operating principle of a molten carbonate fuel cell and the overall reactions are shown. The nominal average operating temperature of a MCFC is 650 °C.

The simple structure of a MCFC is repeated in a stack, as shown in Fig. 2. In a stack, the separator plates divide gases of adjacent cells; provide the electric contact among them and the distribution of reactant gas to the porous electrodes where the reactions take place.

For successful market-entry and competitiveness of MCFC systems, reduction of costs and improvement of reliability and endurance are required.

A limiting aspect for reaching the goal of 40,000 h of life-time is the corrosion of active area of the metallic parts of MCFC, especially in anodic environment. The operating conditions on the anode side, in fact, are more severe and the material must resist to a reducing and carburizing environment at high temperature and in presence of molten carbonates that partially impregnate the anode [2].

Moreover, these materials must be:

- good electrical conductors, i.e. electrically conductive corrosion products;
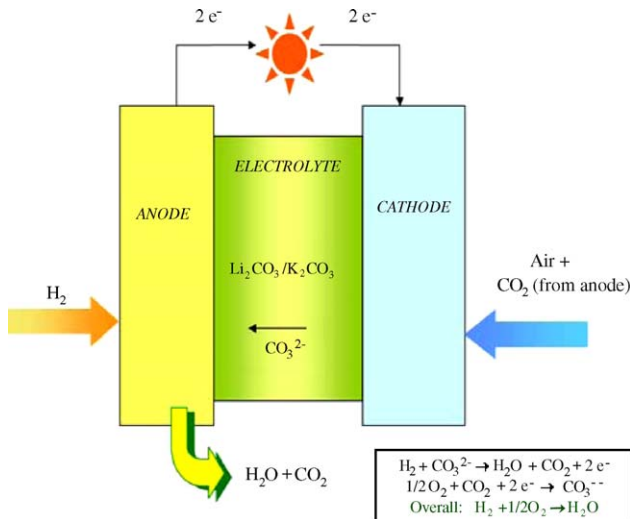- formable into desired shape;
- economically competitive.

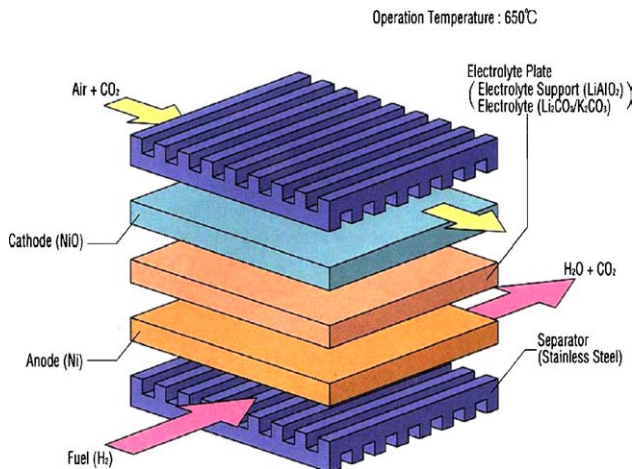Fig. 1. Schematic figure of a MCFC and overall reactions that occur at the electrodes.

Fig. 2. Schematic figure of a molten carbonate fuel cell stack.

2. Experimental methods

To perform corrosion tests, the samples are exposed to Li/K molten carbonate at 650 °C for different time in anodic environment.

The electrical conductivity of oxidized samples, morphology and composition of corrosion layers are investigated.

The samples are exposed to molten carbonate as it is indicated in Fig. 3.

The anodic gas mixture used in the tests was of H_2/CO_2 (80/20) humidified at 50 °C.

The samples, after corrosion tests, have been examined in order to characterize the corrosion behaviour by scanning electron microscope (SEM) equipped with energy dispersive X-ray spectrometer (EDS) and by optical microscope.

The analyses were carried out on the surface of each sample and on the cross section to evaluate the composition of the oxide scale, its thickness, its compactness, internal corrosion, if present, and the conditions of Ni layer [3].
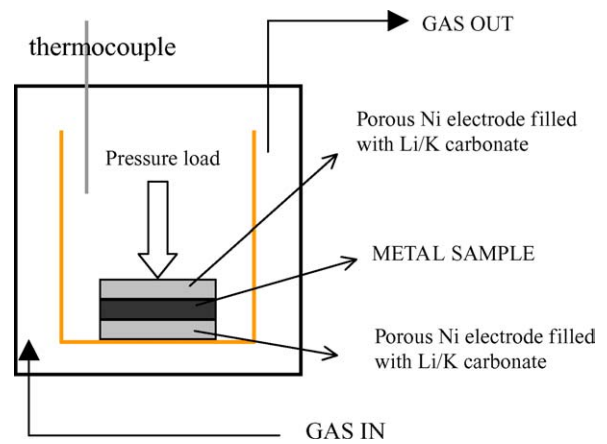

Fig. 3. Schematic arrangement for corrosion tests in anodic environment.

Moreover, the effect of carburization on the different tested alloys is estimated by Vickers micro-hardness measurements through the cross-section.

The consequence of an excessive carburization can provoke an increment of the hardness along the section causing a mechanical failure of the metallic component.

After corrosion tests, the electrical conductivity of the corroded samples are measured by a dedicated high temperature sample holder suited for electrochemical measurements (Fig. 4).

The cell is connected to an ac ohmmeter by four-wire measurements; the measurements are carried out at 1 kHz

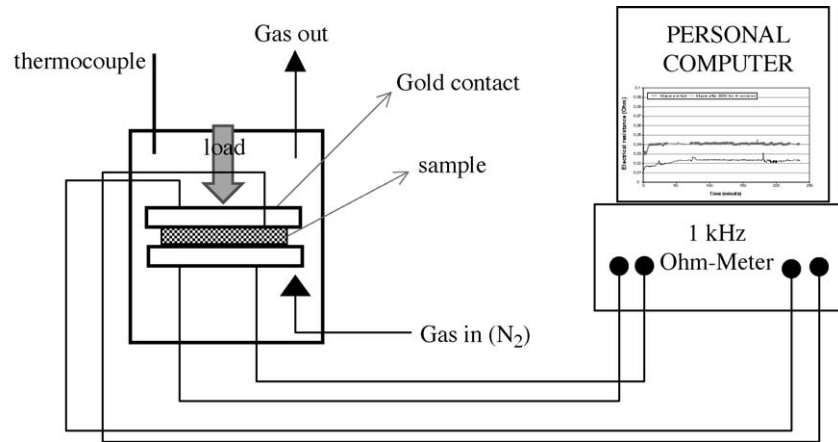Fig. 4. Cell for the measurement of electrical conductivity.

Fig. 5. Schematic drawing of cell connection.

and the data acquisition is made by a personal computer, as shown in Fig. 5.

These measures are carried out on 1 cm × 1 cm samples at 650 °C in presence of high purity N_2 environment, in order to keep the oxide scale unchanged.

3. Results and discussion

The behaviour of a material for anodic metallic components in a MCFC is connected to:

(1) kind of oxide layer grown up on the metal surface;
(2) electrical conductivity of the oxide;
(3) internal corrosion and depletion of the alloy elements beneath the scale;
(4) counter-diffusion across the scale and the protective coatings of oxygen from the gas to the metal and of metal elements to the oxide in combination with scale cracking.
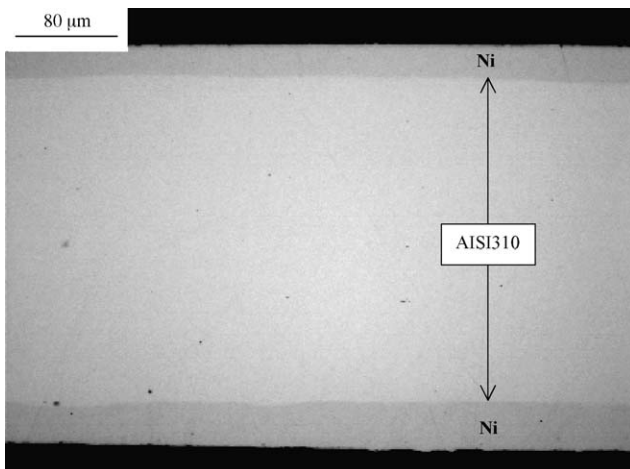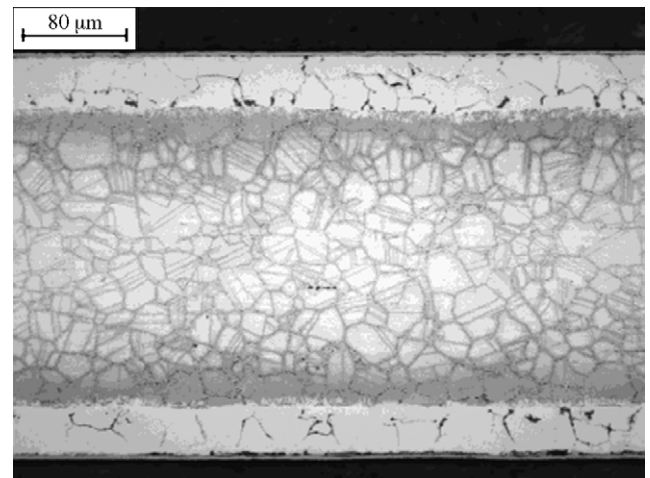

Fig. 7. Trilayer Ni/AISI310S/Ni after 1000 h of corrosion in anodic environment (200×).

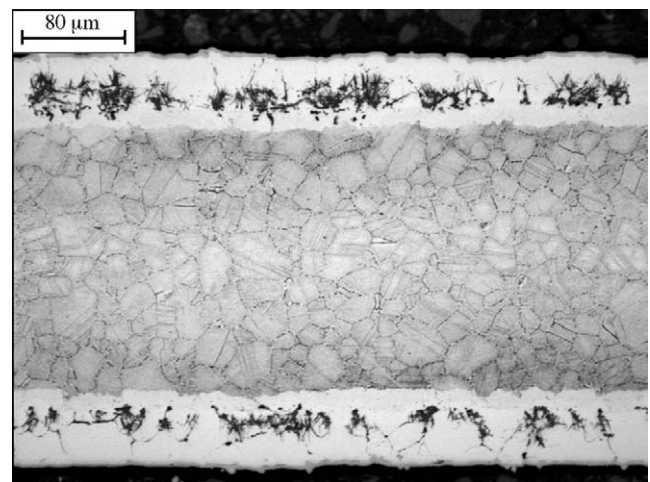Fig. 6. Trilayer Ni/AISI310S/Ni before corrosion tests (200×).

Fig. 8. Trilayer Ni/AISI310S/Ni after 8000 h of corrosion in anodic environment. It is evident the progressive interdiffusion-oxidation processes occurring at the grain boundaries in the Ni coating. (200×).
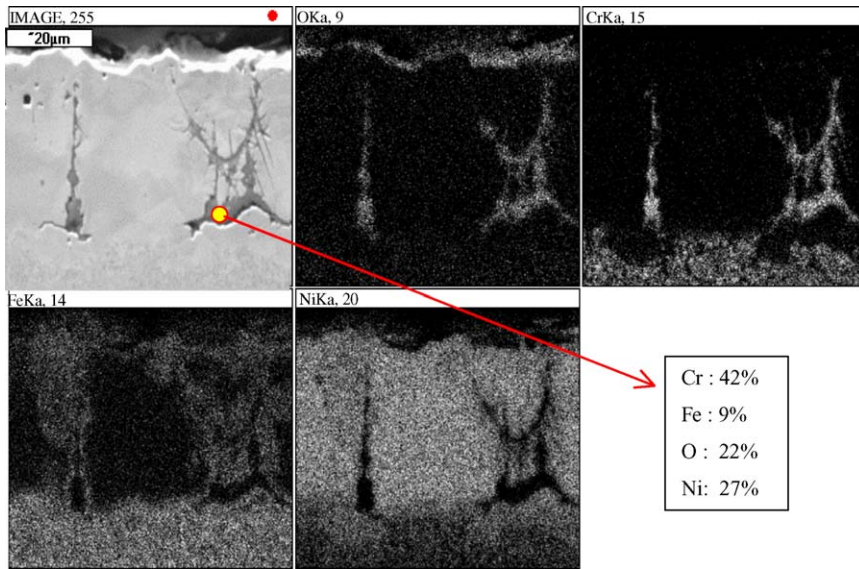
Fig. 9. Map of elements in Ni layer (2000×) after 8000 h of corrosion in anodic environment.

For these reasons, the aim of this study here described was to search out in which way these aspects can damage the Ni/AISI310S/Ni trilayer and cause a loss of efficiency of the collector itself.

The main degradation problems are related to the counter-diffusion of some metal elements (Cr, Fe, Mn) from base material into the nickel coating and of oxidant species (O_2, CO_2) from the external environment [4].

The counter-diffusion occurs through the Ni grain boundaries where Cr and Fe oxidise with a degradation of Ni coating as consequence.

Fig. 6 is related to a sample of trilayer before corrosion test; the thickness of the Ni coating is around 40 μm.

Figs. 7 and 8 are related to trilayer samples after a corrosion test of 1000 and 8000 h. It is evident how the diffusion phenomena through the Ni layer can cause the damage of the protective coating. In Fig. 9, a chemical composition analysis confirms the presence of Cr and Fe oxides along the grain boundaries.

Another problem that influences the behaviour of trilayer in anodic environment is the carburization that affects the base material and leads to a brittleness in the material itself.
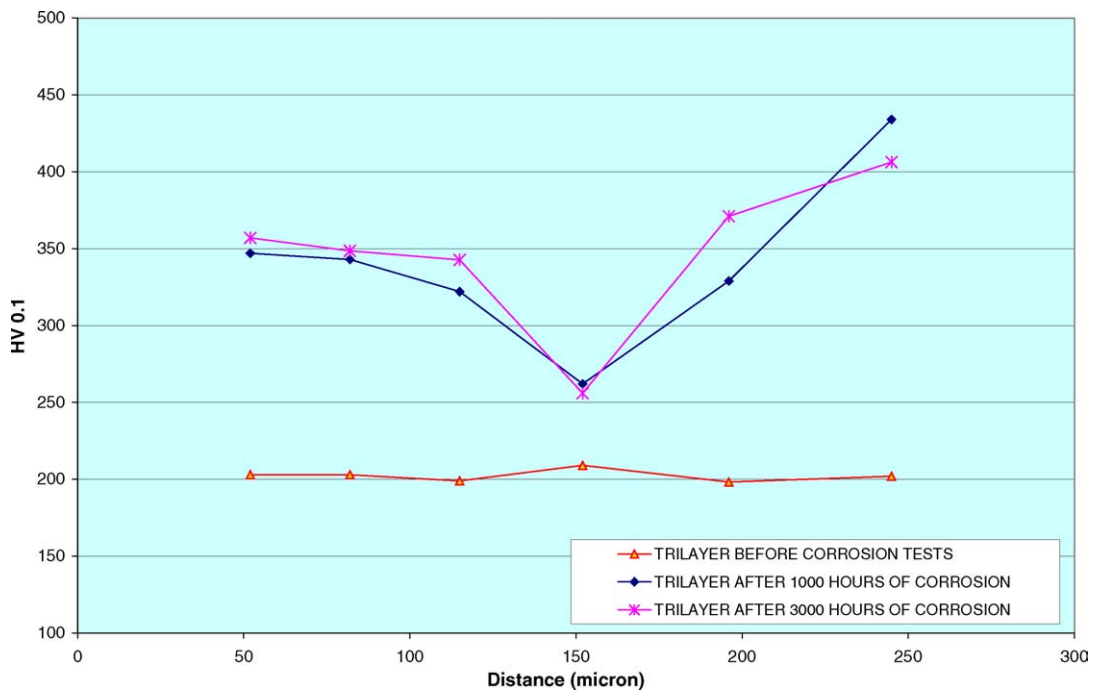

Fig. 10. Effect of carburization on hardness of trilayer in anodic environment.
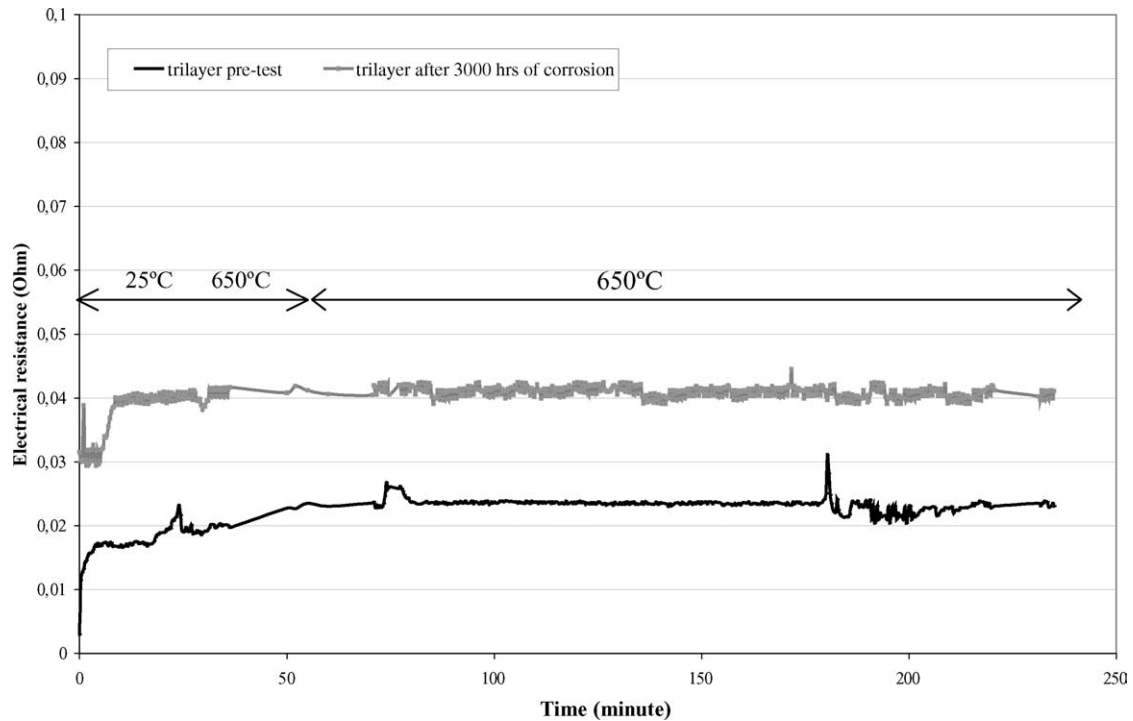
Fig. 11. Electrical resistance of a Ni/AISI310S/Ni trilayer in anodic environment.

The carbon diffuses through the Ni layer and enriches the base metal with a negative increment of hardness.

The measure of Vickers micro-hardness across the section allows to quantify the entity of carburization (Fig. 10). In long term, an increment of the area interested by carburization phenomena occurs. The consequence is an excessive hardness and embrittlement of the metallic component.

About the electrical conductivity, it is another fundamental parameter that must be considered.

In fact, the active area of metallic components must have the lowest as possible electrical resistance.

So, the electrical resistance of samples of trilayer before and after corrosion is evaluated by the cell previously shown.

In Fig. 11, some results obtained in a simulated anodic environment are shown.

After 3000 h in corrosion test, the trilayer shows an increment of the electrical resistance. This can be attributed to the formation of oxides through the Ni grain boundaries. The electrical resistance increment for the trilayer after 3000 h of corrosion is still very low but for longer corrosion time, a further increment could lead to a loss of efficiency of the component itself and, of course, of the whole cell.

4. Conclusion

The combination of good corrosion resistance and an electrically conductive metallic component is quite restrictive. So, the object of the present work is to investigate in which way different aspects connected to the anodic environment in a molten carbonate fuel cell can influence the behaviour and the life-time of some actually used metallic components.

In the anodic environment, the Ni/AISI310S/Ni trilayer is at the moment the material with the highest corrosion resistance for the stability of nickel. At the same time, for long period, a diffusion of elements like Mn, Cr and Fe from the material through the nickel layer to the gas environment can cause a damage in the protective layer and a consequent diffusion of oxygen to the stainless steel.

Further, carburization in the base metal grains or in the grain boundaries beneath the Ni coating has been observed. Therefore, in the long term, carburization can compromise the mechanical characteristics and properties of the metal causing a collapse of the component itself.

Concerning the electrical resistance, an increment has been observed. It is important to investigate, over the long term, the trend of this increment and its influence on the total efficiency of the cell.

References

[1] Fuel Cell Handbook, sixth ed., EG&G Technical Services Inc., U.S. Department of Energy, DE-AM26-99FT40575, November 2002.

[2] P. Capobianco, B. Passalacqua, A. Torazza, Choice of materials for molten carbonate fuel cells and devepment of relevant manufacturing technologies, Mater. Eng. 10 (1) (1999) 25–44.

[3] B. Zhu, G. Lindbergh, D. Simonsson, Comparison of electrochemical and surface characterisation methods for investigation of corrosion of bipolar plate in molten carbonate fuel cell, Corros. Sci. 41 (1999) 1515–1528.

[4] P. Capobianco, P. Guarnone, M. Leonini, A. Torazza, High temperature corrosion in molten carbonate fuel cells for power generation, in: Proceedings of the International AIM/NACE Conference, Venice, May 18–19, 2000, pp. 189–196.