

Short communication

MCFC cathode dissolution: an alternative approach to face the problem

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Abstract

A solution to face the NiO dissolution problem in a molten carbonate fuel cell (MCFC) is hereafter proposed. In particular the performances of a cell in which a matrix layer has been replaced by a ferrite layer are discussed. Process gas analyses, internal resistance, open circuit voltage and $V-I$ plots at constant gas flow and composition are the data collected to assess this technical solution in cell operating conditions.

In addition indications on pre and post-tests analyses are presented in order to underline the most important parameters to verify raw material suitability and the ferrite effectiveness on cathode dissolution.

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1. Introduction

The molten carbonate fuel cell (MCFC) technology is an example of the application of molten salts to the energy production: a proper mixture of alkaline carbonates, which is a melt at the cell operating temperatures, works as electrolyte, taking directly part to the characteristic cell reactions. This fuel cell type is a rather critical and complex system. The cell performances are the result of all the interactions among the different components and the aggressive molten salt environment fixes strict requirements to the materials. This explains the rather slow, but constant, progresses of the MCFC from the pioneer researches on laboratory cells in the seventies [1,2], up to the recent demonstrations of MW class power plants based on stacks of more than 100 cells of about one square meter active area. Refs. [3–5] provide examples of these developments. Nevertheless the present technology still needs improvements to meet the

market requirements. Nickel oxide cathode dissolution has been recognised as one of the most critical factors limiting the cell life, as already explained by Vogel et al. [6] and confirmed by Kasai and Suzuki [7]. Basic researches are still needed to overcome this problem and to increase component endurance and cell performances. Two approaches have been mainly adopted: (i) the substitution of nickel oxide with new cathode materials such as lithium cobaltite or lithium ferrite [8,9]; (ii) the modification and optimisation of the carbonate melt composition, starting from the classic lithium–potassium eutectics [10,11].

The purpose of this paper is to present and discuss results obtained on an alternative approach aimed at improving the cell life by limiting the negative effects of the dissolution of nickel oxide cathodes. The standard AFCo cell package based on a nickel–chromium anode, a multilayer gamma lithium aluminate electrolyte matrix and a lithiated nickel oxide cathode was modified by replacing one matrix layer with a lithium ferrite layer. Single cells were assembled by Ansaldo Fuel Cells (AFCo) and operated at CESI fuel cell laboratory facilities. Encouraging results were obtained from the viewpoint of power density, long-term stability and thermal cyclability. Post test analyses are currently in progress to verify the effectiveness of the ferrite layer in limiting the negative effects of cathode dissolution.

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2. Experimental set up and methods

The single cells used for the present study were realised following a proprietary AFCo design with cross flow configuration. Standard electrodes and housing components were assembled together with the innovative matrix structure. During the assembly, the cell was filled with a proper quantity of alkali carbonate mixture and no refilling was planned in operation. The cell fabrication was concluded by the first heat up (“cell conditioning”) during which the components assumed their final form. The cells were operated at atmospheric pressure with the same reference (REF) gas compositions and flowrates. The fuel gas ($\text{H}_2:\text{CO}_2 = 90:10$) and the oxidant gas ($\text{air}:\text{CO}_2 = 70:30$) were fed. Periodic characterisations were carried out including voltage–current (V – I) characteristics at constant gas flow rates, utilisation curves at constant gas compositions, internal resistance (iR) measurements at 1 kHz and gaschromatographic (GC) analyses on the process gases. The V – I characteristics were recorded by means of an electronic load that fixed current steps and by a voltmeter that measured the cell voltages. The actual currents were measured by using a class 01 shunt. Each V – I characteristic point was maintained for not less than 30' thus allowing a complete thermal stabilisation.

The cell resistance was measured by using a HIOKI 3560 AC m Ω HiTESTER (four wires, 1 kHz). The gas composition and flow rates were controlled by a set of mass flow controllers. GC measurements of the inlet gas mixture compositions allowed us to verify that the mass flow controllers properly operated during long lasting cell runs. GC analyses, however, were mainly devoted to monitor the gas cross-over trend by carefully measuring the amount of hydrogen at the cathode outlet with the cell at open circuit.

A Varian model CP4900 micro-gaschromatograph, was dedicated to the process gas analyses. To avoid “gas matrix” effects, different specific analytical methods were set up for cathode and anode gases, by using gas mixtures of certified amounts of hydrogen, oxygen, carbon dioxide, carbon monoxide and nitrogen.

3. Results and discussion

The study of the lithium ferrite layer effectiveness was carried out on two single cells, indicated as cell A and cell B, that were assembled by Ansaldo Fuel Cells and tested at CESI. A short time run was planned on the former cell to achieve information on the component properties at the beginning of the cell life, just after the complete stabilisation of the performances. A few thousand hours run was planned on the cell B.

3.1. Cell operation and test results

The cell A was fed with dry REF gases and operated at two different current densities (100 and 160 mA cm $^{-2}$). Three V – I characteristics were recorded at $t_{\text{hot}} = 68, 140$ and 259 h. The best results were achieved during the last one, as the cell required about 1 week of hot time to achieve and stabilise the power

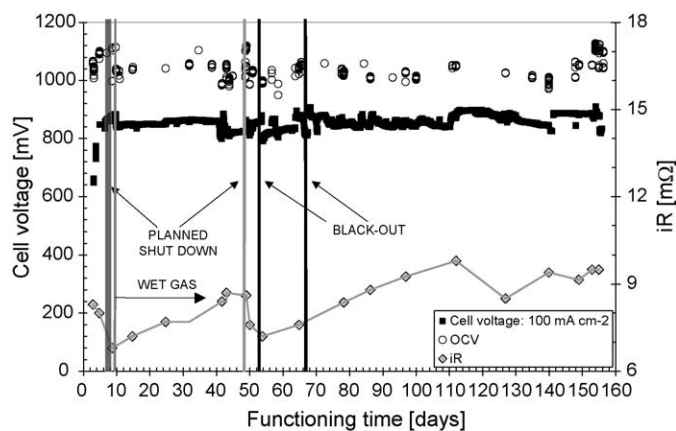


Fig. 1. The cell B life graph. Cell voltage at current density $j=0$ and 100 mA cm $^{-2}$ are reported together with internal resistance measured at 1 kHz.

output. A maximum steady power density of 1.85 kW m $^{-2}$ was obtained on this cell.

A 5.4 m Ω cell internal resistance was measured after 164 hot time hours while the gas cross over appeared to be within acceptable limits. As a matter of fact the hydrogen content in the cathodic outlet stream was significantly less than 1%. The test run was stopped after 315 hot time hours, as soon as stable operating performances were reached.

The cell B accumulated 3751 hot time (t_h) hours (Fig. 1). The cell was operated under a steady load of 100 mA cm $^{-2}$ and fed with wet REF gases, except for the very first part of the operating period (limited by a dashed line in the Fig. 1) when dry REF gases were used. Also this cell required few hundred hours to reach steady performances (Fig. 1). The cell B exhibited slightly lower peak performances with respect to the cell A, but they were quite stable and even slightly increasing during all the operation period. The highest power densities were measured in the last part of the run: 1.54 kW m $^{-2}$ (wet REF gas, $t_{\text{hot}} = 3669$ h) (Fig. 2) and 1.59 kW m $^{-2}$ (dry REF gas, $t_{\text{hot}} = 3694$ h). The absence of power output decay over almost 4000 functioning hours is one of the most remarkable results achieved on this cell. An internal resistance ranging from 7.2 to 9.5 m Ω was measured (Fig. 1). It should be pointed out that the differences between the best

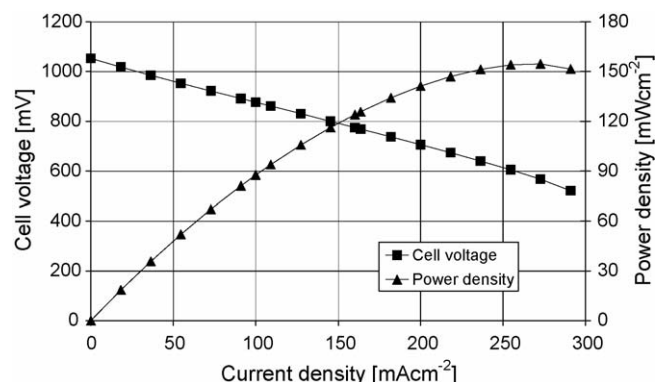


Fig. 2. Voltage and power vs. current density measured on the cell B after 3669 h of hot time.

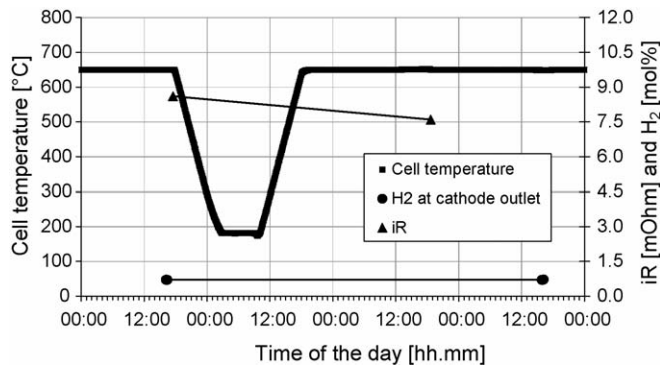


Fig. 3. The cell B behaviour before and after the second planned shut-down.

power densities that were measured on the cell A and the cell B can be mainly ascribed to the higher internal resistance of the latter. The *iR*-free power densities of the two cells differ only of about 5%. The component assembly reproducibility appears satisfactory.

Cell cross over was monitored during the test run mainly by measuring the hydrogen amount at the cathode outlet by gaschromatography. Leakage tests were carried out also by using a bubble meter.

The cross-over was always found within acceptable limits in the cell B. The best results with wet REF gases was obtained after 745 h of hot time.

The cell B was shut down twice (Fig. 1). Specific procedures, provided by Ansaldo Fuel Cells, were carefully applied. *V–I* characteristics, GC analyses and *iR* measurements were performed just before and after the thermal cycles. The electrolyte matrix gas tightness was not affected, while a slight decrease of the *iR* was noticed in both cases (Fig. 3). Similar results were obtained upon two emergency and uncontrolled shut-downs due to electric blackout (Fig. 1).

3.2. Pre- and post-test characterisations of the cell components

The pre-test included the physical chemical characterisation of lithium iron oxide powders. XRD analyses were carried out to control their purity degree, a particle size analyser was used to verify a suitable particle size distribution and the BET technique was applied to measure their specific surface area. Castability tests were executed to balance and set the correct ratio among powders/solvent/binder and additives. The tape cast lithium ferrite green was defect free and after a burn-out it was analysed by the Pascal 140 and Pascal 240 mercury porosimeters: the pore size distribution was that of a typical matrix.

After the operating run the cells were disassembled. In particular, all the cell B active components, as well as the housing metallic ones, exhibited the expected features. Any damage was detected during the visual inspection. Samples were taken for post-test analyses in different cell zones with respect to gas inlet and outlet.

Porosimetric characterisations are currently planned to verify the electrode structure changes and the final filling degree of the

cell. SEM–EDS analyses of the cathode-ferrite-matrix sandwich will be carried out to determine the qualitative Ni concentration profile through the section. The comparison with profiles measured on standard cells with the same operating lifetime will provide information on the ferrite layer effectiveness on Ni dissolution. Nickel quantitative analyses in the ferrite and matrix layers are also planned by means of atomic absorption.

4. Conclusions

Laboratory scale single cells, named cell A and cell B, realised with standard Ni–Cr anodes and NiO(Li) cathodes and an innovative matrix structure including a lithium ferrite layer, were successfully operated for 315 and 3751 h respectively. The following observations were made.

Both the cells reached good performances few hundred hours after the start up, with maximum power densities ranging from 1.53 to 1.85 kW m⁻². This power output was maintained and even slightly improved during the runtime period. The cell B, operated for almost 4000 h without electrolyte refilling, exhibited a 30% increase of the internal resistance. No cell performance decay, however, was noticed.

The innovative matrix structure behaved very well also with respect to thermal cycling. The cell B experienced two planned shut-downs and two partially uncontrolled thermal cycles with electrolyte solidification. Gas chromatographic analyses and internal resistance measurements carried out immediately after these events did not evidence any damage. The post-test characterisation of the components are now in progress to assess the capability of the lithium ferrite layer in minimising the negative effects of nickel oxide cathode dissolution. In any case this innovative technological solution appears promising and the results obtained up to now on single cells justify the further effort required for the scale up at the subscale stack level.

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