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ORIGINAL PAPER

Molten carbonate fuel cell performance under different cathode conditions

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Abstract Molten carbonate fuel cells (MCFCs) are electrochemical devices directly converting chemical energy of a redox reaction into electricity: compared with energy conversion by combustion, it is significantly more efficient and less polluting. This paper presents a preliminary study exploring the possibilities of improving the overall MCFC performances, by lowering the cathode polarization. Tests were carried out on single cell systems: these are devices able to simulate full-size plant operation in its essential features. Single cells are constituted by an assembly of porous and metallic components (anode, cathode, matrix, anodic and cathodic current collectors) enclosed by two steel shells. A particular numerical method were used in order to discriminate between the different contributions (anodic polarization, cathodic polarization, internal resistance polarisation and Nernst losses) to the cell's performance reduction during its operation. This method has been applied to specific single cell test, where only cathode working conditions were changed and the cell's response (in terms of voltage changes) was recorded. In this way the cathode's contribution has been identified. These tests have confirmed the possibility of performance improvement possibilities by working on the cathode polarization.

Keywords Molten carbonate fuel cell (MCFC) · Single-cell test · Cell performance · Cathodic gas composition

List of symbols

K_1	Equilibrium constant of Eq. 7
K_2	Equilibrium constant of Eq. 9
σ	Warburg impedance under semi-infinite diffusion (Ω cm^2/s$^{0.5}$)
R	Gas constant (J/mol K)
T	Temperature (K)
n	Electron number per molecule
F	Faraday constant (C/mol)
C	Concentration (mol/cm^3)
D	Diffusion coefficient (cm^2/s)
Z_N	Nernst impedance under finite diffusion (Ω cm^2)
ω	Angular frequency (rad/s)
δ_N	Nernst diffusion layer thickness
V	Voltage (V)
E	Equilibrium potential or open circuit voltage (V)
η_{ne}	Nernst loss (V)
η_{ir}	Ohmic overpotential drop (V)
η_a	Anode polarization (V)
η_c	Cathode polarization (V)
E^o	Standard equilibrium potential (V)
p	Partial pressure (atm)
R_{iR}	Internal resistance (Ω cm^2)
R_a	Anodic reaction resistance (Ω cm^2)
R_c	Cathodic reaction resistance (Ω cm^2)
J	Current density (A/cm^2)
k_{iR}	Parameter connected to internal resistance (Ω cm^2)
k_a	Parameter connected to anode reaction resistance (Ω cm^2 atm$^{0.5}$)
k_{c1}	Parameter connected to cathode reaction resistance (Ω cm^2 atm$^{0.25}$)
k_{c2}	Parameter connected to cathode reaction resistance (Ω cm^2 atm)

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1 Introduction

A fuel cell is an electrochemical system able to produce electricity: the chemical energy released in a redox reaction is directly converted into electrical energy. Generally, it consists of two electrodes separated by a porous electrolyte matrix; a gaseous fuel is sent to the anode side, where an oxidation takes place, while the oxidant is reduced at the cathode site. The reaction is possible only in the presence of an electrolyte.

Molten-carbonate fuel cells (MCFCs) are high-temperature fuel cells, working at 600–650 °C, adopting molten carbonate salt (Li_2CO_3–K_2CO_3 or Li_2CO_3–Na_2CO_3 mixtures) as electrolyte. Molten electrolyte is retained in a porous, chemically inert ceramic matrix. Typically, fuel is hydrogen or reformed methane and the oxidant is air. The electrochemical reactions occurring in a MCFC involve:

- the formation of carbonate ions ($CO_3^=$) at the cathode by the combination of oxygen, carbon dioxide and two electrons;
- the transport of carbonate ions to the anode through the electrolyte in the matrix;
- the reaction between the carbonate ion and hydrogen at the anode, producing water, carbon dioxide, and two electrons:

Cathode Reaction:

$$CO_2 + 1/2O_2 + 2e^- \rightarrow CO_3{}^= \tag{1}$$

Anode Reaction:

$$H_2 + CO_3{}^= \rightarrow H_2O + CO_2 + 2e^- \tag{2}$$

Overall:

$$H_2 + 1/2O_2 \rightarrow H_2O \tag{3}$$

For each hydrogen mole consumed in the anode compartment, one mole of carbon dioxide and one mole of water are produced.

MCFCs offer many advantages with respect to other fuel cells type:

- Working at high temperatures, MCFCs do not need precious metals (i.e. their catalytic properties) for electrodes realization. In this way electrodes production is less expensive.
- Consequently, it is possible to feed MCFCs adopting a wide range of fuels containing carbon monoxide (e.g. coal gas, waste gas, biomass gas).

Moreover, CO itself can be used as a fuel according to the water gas shift reaction:

$$CO + H_2O = CO_2 + H_2 \tag{4}$$

- High temperature exhausted gas can be used to feed systems like gas or steam turbine in order to improve overall efficiency (up to 85%).
- MCFCs might help to meet the emerging requirement for the reduction of CO_2 content in the atmosphere, by their utilization as CO_2 concentrators/separators: actually, many research efforts are focused on it.

Presently, MCFCs technology is in a pre-commercial phase: one of the main questions still to solve is that of durability, which is affected by factors like high working temperatures and the corrosive behaviour of the electrolyte. Research is concentrating itself both on new corrosion-resistant components as well as new fuel cell designs that increase cell life without decreasing performance. The main goal for commercialization is a 40.000 h (more than 4 years) durability.

The other important problem to solve is cost reduction, including components production and conditioning process charges; it is also very important to increase the overall MCFC performance, which depends on some main parameters as working condition, internal, anodic and cathodic polarization.

2 Cathode polarization

The electrochemical performance of single-cell can be evaluated by studying a polarization curve.

Being the cathodic polarization the most significant contribution to the cell polarization, it is necessary to decrease its value in order to obtain a performance increase.

In fact, while hydrogen diffusion into the carbonate melt and its oxidation are simple and fast phenomena, the cathodic reaction, involving diffusion and reduction of oxygen, is slow and its mechanism complicated.

According to the cathodic reaction:

$$\tfrac{1}{2}O_2 + CO_2 + 2e^- \rightarrow CO_3{}^= \tag{5}$$

In order to explicate the influence of reactant gases on the cathodic reaction resistance, the following simultaneous diffusion mechanism of superoxide ions $O_2{}^-$ and CO_2 in the melt may be assumed [1]:

$$3O_2 + 2CO_3{}^{2-} = 4O_2{}^- + 2CO_2 \tag{6}$$

$$[O_2{}^-] = K_1 \cdot p_{O_2}^{0.75} \cdot p_{CO_2}^{-0.5} \tag{7}$$

$$O_2{}^- + 2CO_2 + 3e^- = 2CO_3{}^= \tag{8}$$

$$[CO_2] = K_2 \cdot p_{CO_2}^{1.0} \tag{9}$$

In a cynetical study [2–4] of the cathodic reaction, the Warburg coefficient was determined by means of impedance measurements at a gold flag electrode: simultaneous diffusion of O_2^- and CO_2 was the dominant feature of mass transport associated with the oxygen reduction, while the charge transfer resistance associated with the effect of the activation process was very small compared with the effect of diffusion (Warburg) impedance.

The Warburg coefficient under condition of semi-infinite diffusion is given as:

$$\sigma = \sum_i \frac{RT}{n_i^2 \cdot F^2 \cdot \sqrt{2}} \cdot \left(\frac{1}{C_i \cdot \sqrt{D_i}} \right) \tag{10}$$

Since electrode reaction occurs in porous sites partially flooded by the electrolyte, the current associated with the electrochemical reaction is concentrated in a film region, thus reactant or product species diffuse in a finite layer (Nernst diffusion).

Thus, the Nernst impedance, corresponding to the Warburg impedance under finite diffusion, is expressed as [5]:

$$Z_n[i] = \sigma_i \frac{1-j}{\sqrt{\omega}} \tanh\left(\delta_N \sqrt{\frac{j \cdot \omega}{D_i}} \right) \tag{11}$$

When ω approaches 0, the only real term of Eq. 11 is:

$$R_d[i] = \lim_{\omega \to 0} Z_N[i] = \frac{R \cdot T \cdot \delta_N}{n_i^2 \cdot F^2 \cdot C_i \cdot D_i} \tag{12}$$

The kind of dependence of R_d on partial pressure through the concentration term C_i, is the same one of the Warburg coefficient.

According to the above mentioned simultaneous diffusion mechanism of superoxide ions O_2^- and CO_2, the cathode reaction resistance can be represented as follows:

$$R_C = R_d[O_2^-] + R_d[CO_2] = k_{c1} \cdot p_{O_2}^{-0.75} \cdot p_{CO_2}^{0.5} + k_{c2} \cdot p_{CO_2}^{-1.0} \tag{13}$$

where k_{c1} and k_{c2} are constants including all the factors, with the exception of partial pressure.

3 Potential balance

For each value of current density, the difference between the open circuit voltage and the measured voltage can be broken down in anodic, cathodic, internal polarization and Nernst loss (due to gas dilution during the reaction) [1, 6, 7]:

$$V = E - \eta_{ne} - \eta_{iR} - \eta_a - |\eta_c| \tag{14}$$

where [8]

$$E = E^\circ + \frac{R \cdot T}{2 \cdot F} \ln\left(\frac{p_{H_2} \cdot p_{O_2}^{1/2}}{p_{H_2O}} \right) + \frac{R \cdot T}{2 \cdot F} \ln\left(\frac{p_{CO_2,c}}{p_{CO_2,a}} \right) \tag{15}$$

To describe the relation between the voltage and the current density it's possible [1, 6, 7] to rewrite (14) as:

$$V = E - \eta_{ne} - (R_{iR} + R_a + R_c) \cdot J \tag{16}$$

where each polarization term is given as depending from the associated resistance (Fig. 1)

The resistance indicated in (16) can be expressed as a function of the reacting gases partial pressures and of temperature [6].

$$R_{iR}(T) = k_{iR}(T) \tag{17}$$

$$R_a(T) = k_a(T) \cdot p_{H_2}^{-0.5} \tag{18}$$

$$R_c(T) = k_{c1}(T) \cdot p_{O_2}^{-0.75} \cdot p_{CO_2}^{0.5} + k_{c2}(T) \cdot p_{CO_2}^{-1.0} \tag{19}$$

Hence it is possible to rewrite (16) in the following way:

$$V = E - \eta_{ne} - [k_{iR}(T) + k_a(T) \cdot p_{H_2}^{-0.5} + k_{c_1}(T) \cdot p_{O_2}^{-0.75} \cdot p_{CO_2}^{0.5} + k_{c_2}(T) \cdot p_{CO_2}^{-1.0}] \cdot J \tag{20}$$

In order to correctly evaluate the coefficients (each connected with a resistance phenomenon), it is necessary to study the local gas compositions and the distribution of current density on the cell plane: for this purpose, it is necessary to ideally divide the cell plane into many different sections (of equal area), as showed in Fig. 2: where in each tiny section the gas composition is assumed constant and therefore the Nernst loss can be neglected. Typically, in this kind of calculation, the cell plane is divided in 100 sections.

So (16) becomes:

$$V = E(i,\ j) - [R_{iR} + R_a(i,j) + R_c(i,\ j)] \cdot J(i,\ j) \tag{21}$$

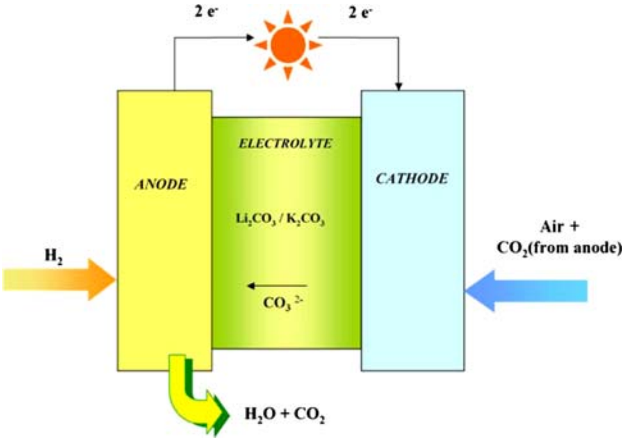

Fig. 1 Scheme of a MCFC and overall reactions occurring at the electrodes

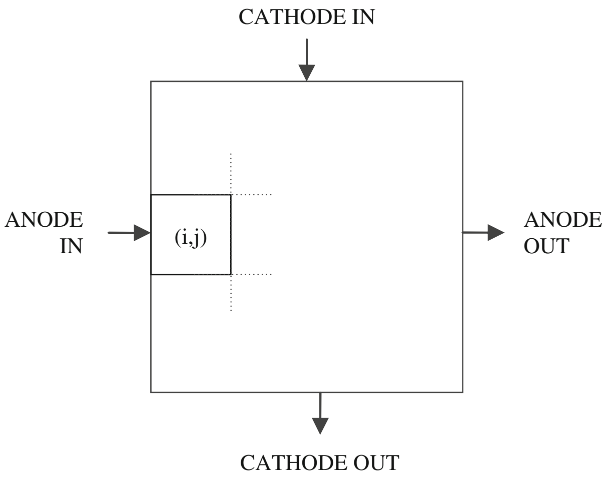

Fig. 2 Representation of section (i, j) on the cell plane

and, consequently:

$$V = E(i,j) - \left[k_{iR} + k_a \cdot p_{H_2}^{-0.5}(i,j) + k_{c1} \cdot p_{O_2}^{-0.75}(i,j) \cdot p_{CO_2}^{0.5}(i,j) + k_{c2} \cdot p_{CO_2}^{-1.0}(i,j)\right] \cdot J(i,j) \qquad (22)$$

where (i, j) are the coordinates of a single section; the voltage term has no indexes because the current collectors ensure the potential uniformity in the cell. The temperature is considered homogeneous throughout the cell plane.

Through the calculation of current density and reactants partial pressure distribution, it is possible to determine the value of electrode polarizations by measuring the cell voltage under fixed current value and gas composition.

4 Experimental and results

The experimental data were collected using a small size single-cell system, composed by porous and metallic materials.

The porous components, cathode and anode, were constituted by Ni-based materials, while the matrix were $LiAlO_2$; the electrolyte was a carbonate salts mixture.

The metallic components, cathodic current collector and anodic current collector were constituted, respectively, by AISI310S and Trilayer Ni/AISI310S/Ni.

A single-cell test facility allows to control the temperature through heating plates, the gas flows through mass flow controllers, the current supply through a electric load.

Moreover, a test facility allows to monitor, control and acquire the most important cell parameters, like voltage, current, temperature, gas flows and differential pressures.

Single-cell tests, through comparative analysis of their results, allow to evaluate the performance change associated with different cathodic gas compositions.

In order to evaluate the electrode polarizations by means of numerical analysis of the potential balance, it is necessary to measure the cell voltage variations associated with changes of the reactants partial pressures and utilization factors at fixed value of current density; besides, the measurement of internal resistance is also required. To carry out this kind of measurement, which quantifies the electrolyte and contact resistance, a milliohmeter, processesing the current response under a fixed voltage frequency signal, was connected to the cell.

Two types of tests (from here on called “A” and “B”) were carried out: in both, a stoichiometric quantity of reactants was provided for the reaction; the used utilization factors of anodic hydrogen and cathodic carbon dioxide and oxygen were the same.

The test A was carried out under the following conditions:

- temperature: 650 °C;
- absolute pressure: 1 atm;
- composition of anodic gas: H_2 64%, CO_2 16%, H_2O 20%;
- composition of cathodic gas: O_2 33%, CO_2 67%.

The measured value of iR was 12.3 mΩ while the differential pressure between anode inlet and cathode inlet was about 0 mbar.

The test was run at three different values of current density (50, 100 and 150 mA/cm^2) and the electrode polarizations, obtained through the above explained analysis, are shown in the Fig. 3.

It is possible to notice that the cathodic polarization value is only slightly affected by a current density increase, so that the relative iR free voltage remains high.

The test B was carried out under the following conditions:

- temperature: 650 °C;
- absolute pressure: 1 atm;
- composition of anodic gas: H_2 64%, CO_2 16%, H_2O 20%;
- composition of cathodic gas: Air 70%, CO_2 30%.

The measured value of iR was 13.3 mΩ while the differential pressure between anode inlet and cathode inlet was about −0,5 mbar.

The differential pressure influence on the result of both test A and B, was considered negligible.

The test was run at three different values of current density (50, 100 and 150 mA/cm^2) and the electrode polarizations, obtained through the above explained analysis, are shown in the Fig. 4.

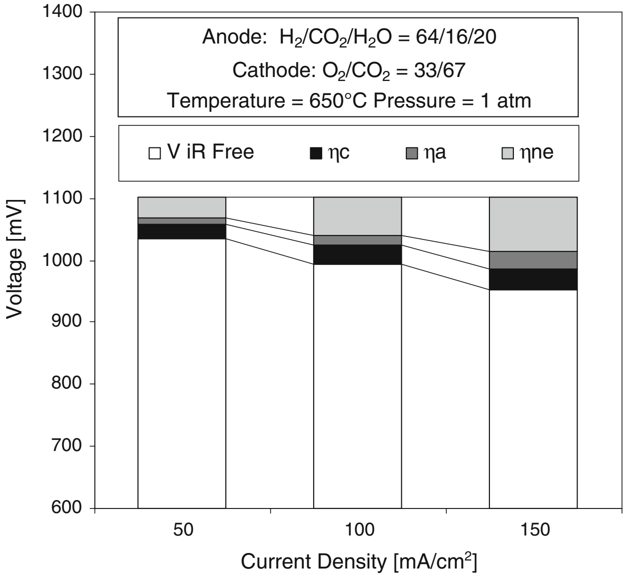

Fig. 3 Test A—Analysis of cell performance under different values of current density

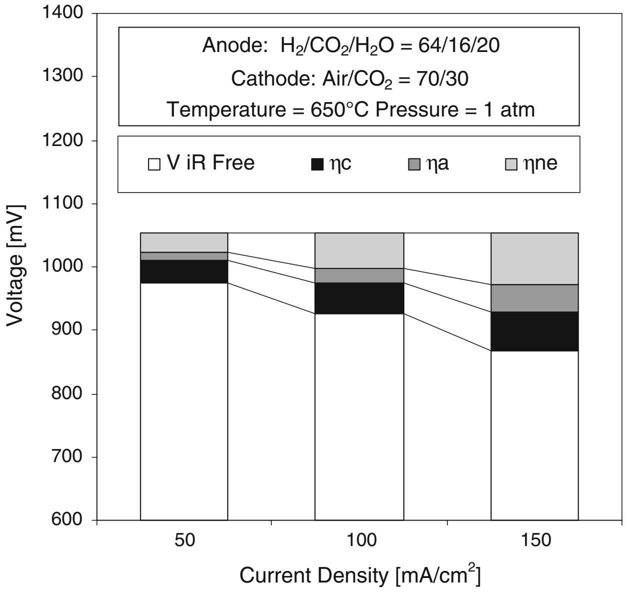

Fig. 4 Test B—Analysis of cell performance under different values of current density

As can be seen in Fig. 4, the cathodic polarizations obtained in test B were not only of higher magnitude than those previously obtained in test A, but showed a perceptible rise with the current density increase, so that the resulting output iR free voltage reduction was considerable.

To help interpret the obtained results, the values of output voltage measured in both tests at different current densities are shown in Fig. 5.

The translation of the two curves is due to a different open circuit voltage (which is, as shown in Eq. 15, function of the reagents partial pressure), while the slope difference is due to the changes in polarization.

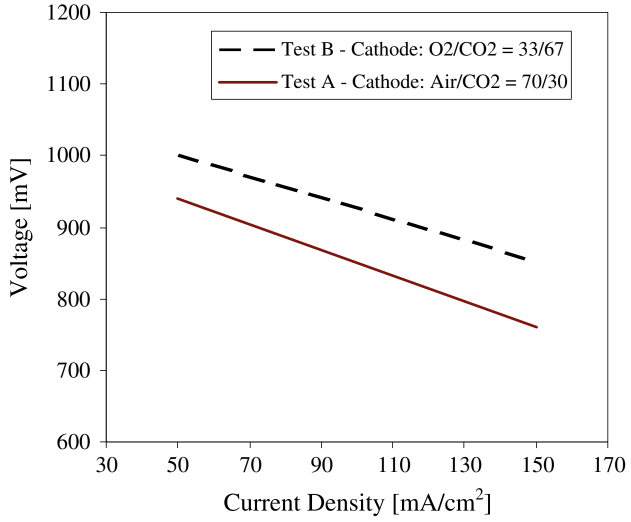

Fig. 5 Performance curves under different cathode conditions

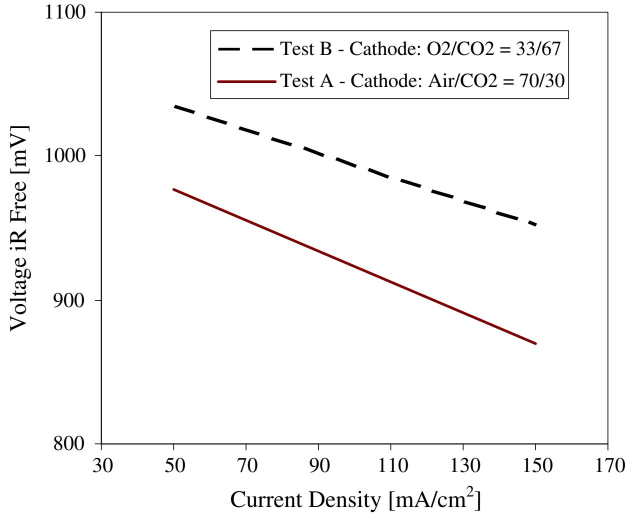

Fig. 6 Performance curves iR Free under different cathode conditions

To better appreciate the improvement of performance due to a cathodic polarization decrease, the output voltage measured has been corrected: such correction is due to an internal resistance value increase in test B (the anodic polarization being similar); so the iR Free Voltage curves are shown in Fig. 6: in this case, the slope difference is due only to the change in cathodic polarizations.

5 Conclusions

Tests performed on a single-cell have confirmed the possibility of improving the performance working on the cathode polarization. Indeed, cathodic polarization is, at the electrode level, the main cause of decreasing output voltage under current load.

According to the test results, it could be suggested that cathode polarization may be reduced adopting a cathodic gas devoid of nitrogen: gas dilution, due to the ratio O_2/N_2 in the air, has an effect on cell performance reduction. It should be taken in account that, since oxygen and carbon dioxide utilization factors in tests A and B were the same, an important role is also played by the reactant gases partial pressures (0.67 and 0.33 atm in test A, 0.30 and 0.15 atm in test B for carbon dioxide and oxygen, respectively).

Besides, according to the results, while in test A the value of cathodic polarization was apparently just slightly depending on the current density value, in test B each variation of current density was accompanied by a significant variation of cathodic polarization: probably, this fact is due to the presence of an inert gas (not involved in the reaction) in the cathodic feed: increasing the current density, reactants are consequently increasingly consumed, therefore the quantity of available oxygen and carbon dioxide in the cell decreases, and dilution becomes increasingly important. This because the presence of the diluting inert gas negatively affects the diffusion process of the reactants in the molten carbonate film region and the relative polarization grows.

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