

The dynamic performance of a molten carbonate fuel cell in power-generation systems

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Abstract

This paper is devoted to the analysis of the dynamic performance of a molten carbonate fuel cell operating in power-generation systems. Fundamental techniques for modelling the molten carbonate fuel cell are proposed. More specifically, the modelling takes account of the dominant mass-flow, chemical reaction, voltage-current and heat-transfer processes. The transient responses of the main parameters (such as temperature and electrical current) of the fuel cell with respect to load variations are presented.

Keywords: Fuel cell; Power-generation system

1. Introduction

In order to meet energy demands as well as preserve the global environment, maximum effort is required to seek more efficient and environmentally friendly energy technologies. Still a maturing technology, a fuel-cell power-generation system (FCPGS) has indicated advantages over conventional power-generation systems.

A fuel cell converts the energy of a chemical reaction directly into electrical energy. The process involves the oxidation of a fuel (such as hydrogen) and the reduction of an oxidant (usually oxygen). Fuel cells offer several potential advantages over conversional energy-conversion systems: substantially higher conversion efficiency of fuel energy to electrical energy, modular construction, high efficiency at partial load operation, minimal siting restrictions, potential for co-generation (simultaneous production of heat and electrical power) and much lower production of pollutants. Referring to the lower heating value of hydrogen, the theoretical electrical efficiency of a fuel cell reaches approximately 90% at 100 °C, and approximately 70% at 1000 °C [1]. The theoretical efficiency of a fuel cell is not subject to the Carnot limitation imposed on heat engines. Now the fuel cell, enormously improved over the spacecraft version, appears to have reached a stage where it can make a significant contribution to a nation's supply of electricity.

The dynamic and controllable behaviour of an FCPGS operating with a variable load is of great interest in its commercial realization in the electrical power industry. An FCPGS features a high level of integration of various components (including new applications for traditional components, and entirely new components). The performance of a complete FCPGS depends on the performance characteristics of the individual components or subsystems and the matching among the components. The complexity of an FCPGS may cause dynamic interactions that are difficult to predict.

Secondly, the development of large-capacity fuel-cell stacks (e.g., 250 kW) is an ongoing technology in the FCPGS. The electrical power from the fuel-cell stack is used to track directly the variation of consumer loads or can be used in conjunction with the electrical grid. Therefore, the dynamic performance of the stack is of great interest for efficient and safe operation. Moreover, a dynamic analysis can provide a basis for improvement of the fuel-cell stack design and its control technology. In view of the operating complexity of a fuel-cell stack and the potential for recycling techniques (that further increase the efficiency of the whole FCPGS), the study of control strategies for effective and economical operation will continue to be a challenging research topic.

Thirdly, electrical load changes are important and frequent occurrences in any power system. Since the FCPGS can be subject to step and ramp changes in

load, an understanding of the effects of transient conditions on the FCPGS's performance is essential for its optimal design and control.

Moreover, most components will work over a wide range, while a FCPGS operates in a load-following mode. Hence, testing each component individually and matching them on real systems to explore the full performance of a complete FCPGS can be both very costly and extremely laborious. Therefore, simulating the dynamic performance of an FCPGS on a computer has obvious advantages. However, there are only a few effective tools available for analysing the dynamic behaviour and control of the complete FCPGSs in existence today.

The factors mentioned above form the primary motivation of the project entitled 'Dynamic modelling and control of integrated fuel cell systems' at the Laboratory of Thermal Power Engineering, Delft University of Technology. This project emphasizes the development of an effective tool for analysing the dynamic behaviour and control of a complete FCPGS. The results from this study are expected to be applicable to the two 250 kW molten carbonate fuel cell (MCFC) system demonstration projects scheduled for operation in the Netherlands in 1995/1996. The general approach of this project and the stationary performance of the reformer have been partly presented in Ref. [2]. This paper will emphasize the dynamic performance of the MCFC at system level. The fuel-cell type is restricted to the MCFC, thus, without further specification, the term 'fuel cell' in this paper refers to an MCFC.

The MCFC studies were constructed using the recent comprehensive plant-modelling code SpeedUp [3].

2. Process description

The fuel cell consists of two porous electrodes separated by a molten carbonate electrolyte, which serves to conduct carbonate ions from the cathode (the oxidant electrode) to the anode (the fuel electrode). The fuel for the MCFC is a mixture of H_2 and CO and the oxidant is a mixture of O_2 and CO_2 . Fuel cells are not operated as single units; rather they are stacked one on top of the other to build up voltage. Fuel-cell stacks are operated at a temperature of about 650 °C, and at a pressure between 1 and 10 bar.

Fuel-cell operation is the result of a complex conjunction of physical and chemical processes. Here modelling attention is focused on the outputs potentially relevant for the dynamic behaviour of the FCPGS. Hence, we shall be especially concerned with the processes involving mass flow, chemical reaction, voltage-current characteristics and heat transfer. All these processes take place simultaneously.

2.1. Mass-flow process

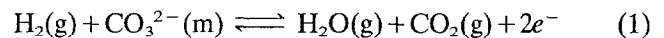
The reactant gases, fuel and a gas mixture of air and CO_2 , are separately fed to the anode and cathode manifolds in the fuel-cell stack. At the anode and cathode inlet manifolds, the gases are transported along the stacking direction. Further, in the cell anode and cathode flow paths, the gases flow from the inlet manifold to the outlet manifold. At the anode and cathode outlet manifolds, the gases exit along the stacking direction.

In the fuel-cell flow path at cell level, adsorbed CO_2 and O_2 on the cathode side react to form CO_3^{2-} , which reacts at the anode side with adsorbed H_2 to form H_2O and CO_2 , and release electrons.

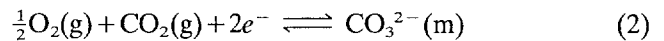
2.2. Chemical reaction process

The electrochemical reactions considered at the fuel-cell electrodes are the following:

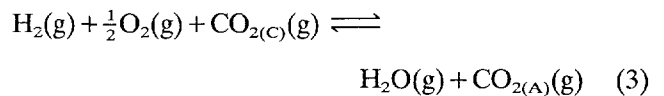
at the anode:



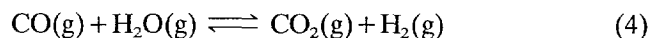
at the cathode:



The overall cell reaction reads:



On the anode side, the water-shift reaction also occurs, increasing the H_2 concentration:



2.3. Voltage-current characteristic

The maximum electrical work obtainable (W_{ei}) in a fuel cell operating at constant temperature and pressure is given by the change of the Gibbs free energy (ΔG) of the electrochemical reaction:

$$W_{ei} = \Delta G = -nFE \quad (5)$$

The maximum electrical voltage obtainable (E) in a single fuel cell, which is often called the reversible cell potential, is given by the Nernst equation (6). For the overall cell reaction, the cell potential increases with an increase in the activity of reactants and a decrease in the activity of products. Changes in temperature also influence the reversible cell potential.

$$E = E^0 + \frac{RT}{2F} \ln \frac{y_{H_2} y_{O_2}^{1/2} y_{CO_2(C)}}{y_{H_2O} y_{CO_2(A)}} + \frac{RT}{4F} \ln P \quad (6)$$

However, the working voltage (V) for a fuel cell is much lower than the Nernst potential. There are ir-

reversible losses in a practical fuel cell. These losses primarily stem from three sources: (i) ohmic polarization; (ii) concentration polarization; and (iii) activation polarization [4].

$$V = E - \eta_{\text{ohm}} - \eta_{\text{conc}} - \eta_{\text{act}} \quad (7)$$

2.4. Heat-transfer process

The generation of heat in a fuel cell is a measure of its inefficiency, but it is also of cardinal importance for applications such as co-generation. It is helpful to distinguish two types of generated heat. One is the heat associated with the reversible cell reaction. The other is the ‘irreversible’ heat, caused by resistance to current passage. In conventional stacks, operating on externally reformed natural gas, significant removal of heat is necessary to maintain the stack temperature at about 650 °C.

There are conductive, convective and radiative heat-transfer phenomena between fuel at the anode-side compartment, the electrolyte matrix and air at the cathode-side compartment in the fuel cell.

At this stage an overall model of the fuel cell may be set up, in which the whole fuel-cell stack is considered as an equivalent large fuel cell. For analysing the heat-transfer processes, this large cell is considered to consist of three elements: fuel, cell and air. A uniform temperature distribution in each element is assumed.

In the fuel element, heat is generated by the water/gas-shift reaction and there is a comprehensive heat transfer from the fuel element to the cell element. This comprehensive heat transfer means the total transfer of conductive, convective and radiative heat.

In the cell element, the heat factors include: (i) heat from the overall electrochemical reaction; (ii) electricity generation; (iii) the comprehensive heat transfer from the fuel element to cell element; and (iv) the comprehensive heat transfer from the cell element to the air element.

In the air element, there is a comprehensive heat transfer from the cell element to the air element.

3. Main dynamic equations

3.1. Assumptions

The fuel-cell stack consists of a number of series-connected cells. These cells are considered to have the same performances, e.g., temperature and current distribution. With this assumption, the analysis of a fuel cell at stack level is reduced to the analysis of a fuel cell at cell level.

The analysis of the dynamics of a fuel cell is at present based on lumped modelling, which assumes

that the physical and chemical properties of the streams are at one operating condition, such as the mean temperature and pressure.

3.2. Mass balance

The overall mass of the fuel-gas layer at the anode side of a fuel cell can be written as:

$$\begin{aligned} & \text{flow}_{A_{\text{in}}} - \text{flow}_{A_{\text{out}}} + \text{stoich}_{1} \text{rate}_1 + \text{stoich}_{A_2} \text{rate}_2 \\ & = \frac{V_A}{W_A} \frac{d(\rho_A v_A)}{dt} \end{aligned} \quad (8)$$

The composition balance of the air layer on the cathode side of a fuel cell is readily derived as

$$\text{flow}_{C_{\text{in}}} - \text{flow}_{C_{\text{out}}} + \text{stoich}_{C_2} \text{rate}_2 = \frac{V_C}{W_C} \frac{d(\rho_C v_C)}{dt} \quad (9)$$

3.3. Energy balance

In accordance with the heat-transfer process considered earlier, a general energy balance for fuel, cell and air elements, respectively, can be formulated as follows:

$$\begin{aligned} & F_{A_{\text{in}}} h_{A_{\text{in}}} - F_{A_{\text{out}}} h_{A_{\text{out}}} + \text{heat}_1 - \text{heat}_{AF} \\ & = \frac{V_A}{W_A} \frac{d(\rho_A h_A)}{dt} \end{aligned} \quad (10)$$

$$\text{heat}_2 + \text{heat}_{AF} - \text{heat}_{FC} - P_{\text{el}} = M_{\text{cell}} C_{p_{\text{cell}}} \frac{dT_{\text{F}}}{dt} \quad (11)$$

$$F_{C_{\text{in}}} h_{C_{\text{in}}} - F_{C_{\text{out}}} h_{C_{\text{out}}} + \text{heat}_{FC} = \frac{V_C}{W_C} \frac{d(\rho_C h_C)}{dt} \quad (12)$$

In order to get a useful solution, quite a lot of algebraic equations are required to balance the total number of unknown variables to the total number of equations. These algebraic equations describe the physical laws of the mass-flow, voltage-current and heat-transfer processes of the fuel cell, the chemical reaction kinetics and the physical properties (for details see Ref. [5]).

4. Program implementation

The present fuel-cell model was implemented in the SpeedUp code. SpeedUp is a recent tool for comprehensive process modelling and it has the following three significant features:

1. SpeedUp is a flowsheeting package, which is designed to model processes as they occur in chemical or process engineering environments as a series of unit operations interconnected by process streams.

2. The SpeedUp simulation allows steady-state and dynamic runs to be carried out using the same software tool and the same program input. This also means that the results of stationary simulations can be used to initialize the dynamic simulations.

3. SpeedUp can effectively deal with explicit and implicit differential and algebraic equations.

According to the author's program-implementation practice, divergencies are the usual cause of failures during the steady-state simulation. It is found that an accurate estimation of the major variables' minimum and maximum limits or setting proper default values may effectively help steady-state simulation convergence. Moreover, matrix singularity is the usual cause of failures during dynamic simulations and it is found that reformulating some equations by considering causal relations between the major variables may reduce the possibility of matrix singularity. The dynamic simulation of the fuel-cell model has been performed on a Sun IPX computer, and leads to the following interesting results.

4.1. Dynamic performance

Open-loop step tests are probably the most straightforward way of investigating the dynamic behaviour. Hence, the responses of the fuel-cell model to step changes of manipulated variables provide valuable insight into the process trends, time scale and static gains. In detail, the fuel-cell model responses to a +10% step change of fuel-gas flow rate will be discussed in the following example. The results depend heavily on the configuration and the properties of the fuel cell.

For more details of the simulation assumptions in the following example, see Ref. [5].

Example: fuel-cell model responses to a +10% open-loop step change of fuel-gas flow rate at anode inlet

In order to get a different electrical power output, manipulating the gas-flow rate at the fuel-cell anode inlet is a frequent occurrence in FCPGS operations. Thus, the responses of the temperature and the electrical parameters to a +10% step change, which are demonstrated in Figs. 1–3, are of great interest for studying FCPGS dynamic performance.

Fig. 1 shows that the temperatures of the fuel gas at the anode side (T_A), the fuel cell (T_F) and the gas at the cathode side (T_C) increase significantly (about 20 K, 3.3%) with respect to a +10% step change in fuel-gas flow rate. These phenomena result from the +10% increase of fuel-gas flow rate at the anode inlet and the constant gas-flow rate at the cathode inlet (one function of the gas at the cathode is to cool the fuel-cell compartment). The increase of temperature also indicates that more conversion has taken place (so more current has been produced), which will be confirmed in Fig. 3. Moreover, the time scale of temperature responses is of the order of 1000 s. It is noticed that the dramatic responses for T_A and T_C occurred at the beginning.

Fig. 2 provides a clear insight into the temperature responses on a small time scale. The temperature of the fuel gas at the anode side (T_A) jumps to a maximum value, drops and subsequently changes very slowly. There is almost no variation in the temperature of the fuel cell (T_F). The temperature of the gas at the cathode

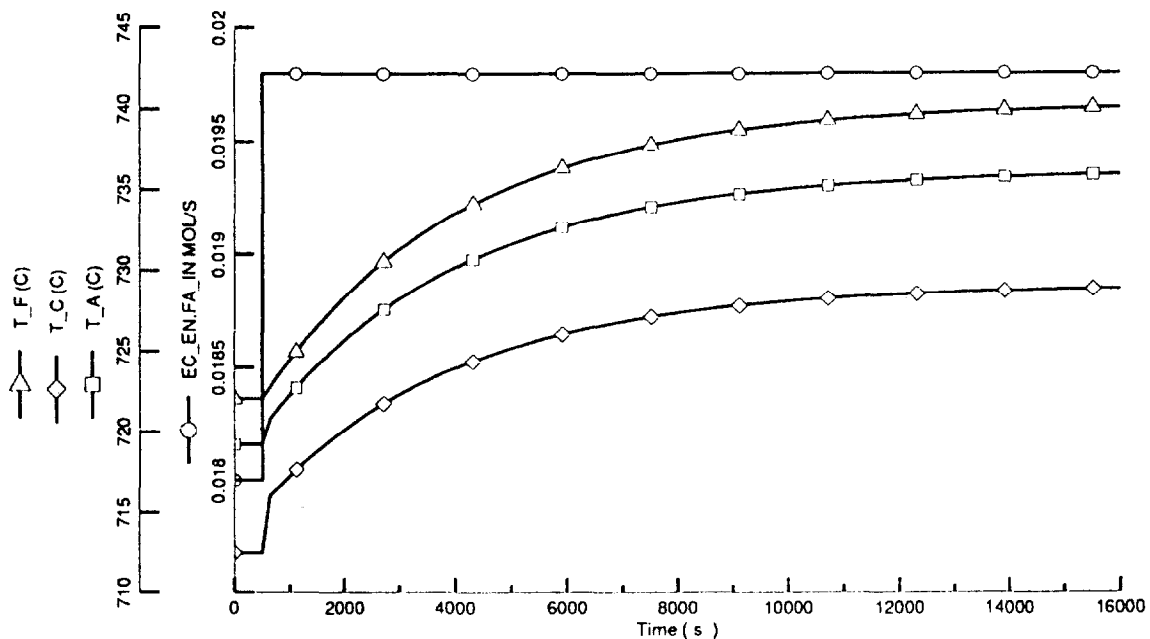


Fig. 1. Temperature responses to a +10% step change of fuel-gas flow rate (on large time scale).

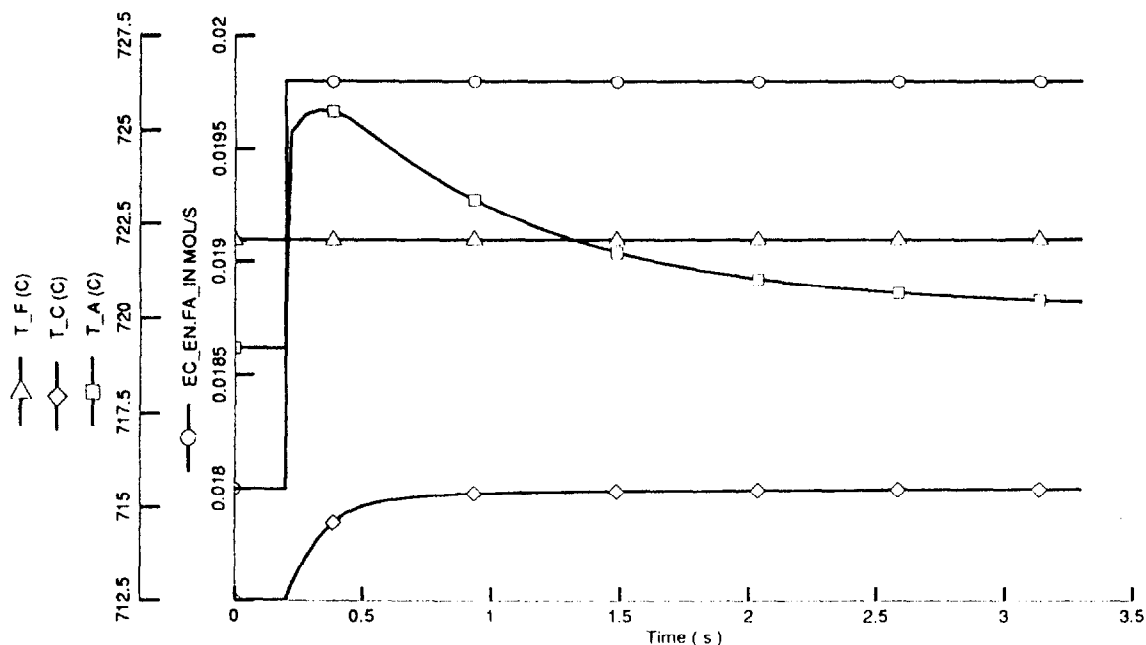


Fig. 2. Temperature responses to a +10% step change of fuel-gas flow rate (on small time scale).

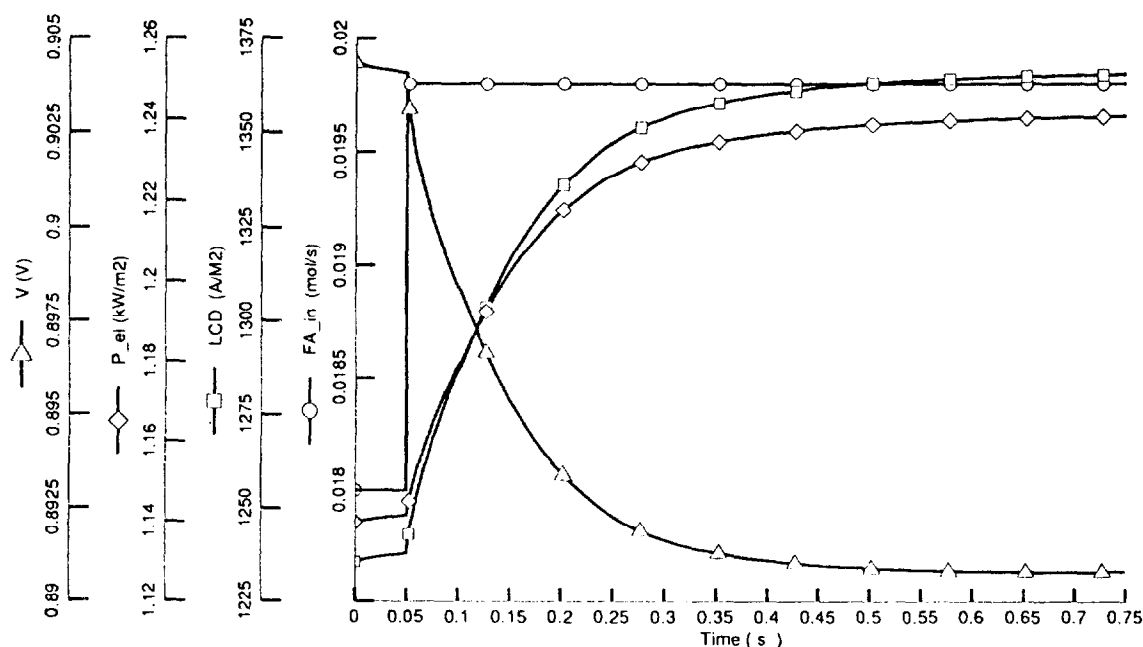


Fig. 3. Electrical responses to a +10% step change of fuel-gas flow rate.

side changes very fast initially, and then changes very slowly. If the temperature maximum for T_A is very high, it may lead to harmful effects on fuel-cell materials. These phenomena are due to the rapid chemical reaction processes and the relatively slow heat-transfer processes.

Fig. 3 illustrates the voltage (V), power density (P_{ei}) and current density (LCD) responses. The current density increases fast and the voltage decreases accordingly (because of irreversible losses). However, there is a net gain of power density (about 0.1 kW/

m², 8.8%), which can reach the required value within a time scale of seconds.

Therefore, the present simulation leads to the conclusion that the temperature responses on a small time scale (seconds) are dominated by the chemical processes, and the temperature responses on a large time scale (1000 s) are dominated by the heat-transfer process. This example also confirms that the manipulation of the fuel flow rates is an effective strategy for changing the output electrical energy from the fuel cell.

5. Conclusions

This paper presents a numerical tool for analysing the dynamic performance of an MCFC in the load-following mode. The dominant phenomena, such as mass-flow, chemical reactions, voltage–current characteristics and heat transfer are modelled, and have been implemented in the SpeedUp code. The transient responses of the main parameters of the fuel cell for the load-following mode have provided valuable insight into the operating characteristics of an MCFC in the FCPGS. Although it has not yet been possible to compare the results obtained by calculations with test data, the trends shown appear to be reasonable.

6. List of symbols

$C_{p_{cell}}$	heat capacity of all fuel-cell materials (kJ/kg)
E	reversible potential of the cell (V)
E^0	standard reversible potential of the cell (V)
F	Faraday constant
F	total gas flow rate (kmol/s)
$flow$	gas flow rate for one composition (kmol/s)
ΔG	Gibbs free energy of the overall cell electrochemical reaction (kJ/mol)
ΔH_{298}^0	standard heat available from reaction (kJ/mol)
$heat_1$	heat generated by water/gas shift, and overall cell reaction (kW)
$heat_2$	overall heat generated by water/gas shift, and overall cell reaction (kW)
$heat_{AF}$	overall weight of the fuel-cell compartment, except that of fuel gas and air (kg)
$heat_{FC}$	number of electrons participating in the reaction
M_{cell}	total pressure (bar)
n	gas constant
P	reaction rates for the shift, and cell electrochemical reactions (mol/s)
R	stoichiometric numbers of the shift reaction
$rate_1$	stoichiometric numbers of the electrochemical reaction at the anode
$rate_2$	stoichiometric numbers of the electrochemical reaction at the cathode
$stoich_1$	temperature (°C)
$stoich_{A2}$	temperature of fuel-cell compartment, except that of fuel gas and air (°C)
$stoich_{C2}$	available cell voltage (V)
T	volume (m ³)
T_F	gas molar weight (kg/kmol)
V	maximum available electrical energy in a fuel cell (kW)
V	gas molar fraction
W	
W_{el}	
y	

Greek letters

η_{ohm}	ohmic polarization (V)
η_{conc}	concentration polarization (V)
η_{act}	activation polarization (V)
ρ	molar density (kg/m ³)

Subscripts

A	lumped parameter for the gas layer on the anode side
C	lumped parameter for the gas layer on the cathode side
A _{in}	parameters for the inlet and outlet on the anode side
A _{out}	parameters for the inlet and outlet on the anode side
C _{in}	parameters for the inlet and outlet on the cathode side
C _{out}	parameters for the inlet and outlet on the cathode side

Abbreviations

FCPGS	fuel-cell power-generation system
g	gas
m	melt
MCFC	molten carbonate fuel cell

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