



Anode supported single chamber solid oxide fuel cells operating in exhaust gases of thermal engine



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HIGHLIGHTS

- A gas mixture representative of engine exhausts atmosphere is used as fuel.
- Anode supported Single Chamber SOFCs are studied at temperatures around 500 °C.
- The prepared cells are able to convert exhaust gas into electricity.
- Materials choice and microstructure optimization leads to better performances.

ARTICLE INFO

Article history:

Received 4 March 2014

Received in revised form

28 May 2014

Accepted 11 June 2014

Available online 18 June 2014

Keywords:

Single chamber SOFC

Energy recovery

Unburned hydrocarbons

Pollutant emissions reduction

ABSTRACT

This project deals with the development and the electrochemical characterization of anode supported single chamber SOFC in a simulated environment of thermal engine exhaust gas. In the present work, a gas mixture representative of exhaust conditions is selected. It is composed of hydrocarbons (HC: propane and propene), oxygen, carbon monoxide, carbon dioxide, hydrogen and water. Only oxygen content is varied leading to different gas mixtures characterized by three ratios $R = \text{HC}/\text{O}_2$. Concerning the cell components, a cermet made of nickel and an electrolyte material, $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (CGO) is used as anode and two cathode materials, $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) and $\text{Pr}_2\text{NiO}_{4+\delta}$ (PNO), are evaluated. The prepared cells are investigated in the various gas mixtures for temperatures ranging from 450 °C to 600 °C. Ni-CGO/CGO/LSCF-CGO cell has delivered a maximum power density of 15 mW cm^{-2} at 500 °C with $R = \text{HC}/\text{O}_2 = 0.21$, while lower power densities are obtained for the other ratios, $R = 0.44$ and $R = 0.67$. Afterwards, LSCF and PNO cathode materials are compared and LSCF is found to deliver the highest power densities. Finally, by improving the electrolyte microstructure, some cells presenting a maximum power density of 25 mW cm^{-2} at 550 °C are produced. Moreover, up to 17% of initial HC are eliminated in the gas mixture.

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1. Introduction

Solid oxide fuel cells are usually described as devices able to convert chemical energy into electrical energy. Conventional solid oxide fuel cells are separated into two compartments containing each electrode split by a gastight electrolyte. Fuel (hydrogen, in most cases) and oxidant (oxygen or air) feed directly each chamber and a special attention is paid to separate carefully the two gases. At the cathode side, oxygen is reduced into oxygen ions (reaction 1) which travel through the electrolyte to the anode side, where

they oxidize hydrogen into water (reaction 2). Electrons produced by hydrogen oxidation are then drawn to the cathode through an external circuit. The overall reaction is the chemical oxidation of hydrogen to water (reaction 3).



Since the early nineties [1,2], SOFC have been studied in a new configuration where anode and cathode are exposed to the same gas mixture in a single chamber. The Single Chamber SOFCs

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(SC–SOFCs) are particularly interesting [3,4] due to the absence of sealing between the two usual compartments, removing one of main challenges of conventional SOFCs. However, in SC-SOFC configuration, hydrogen cannot be used as a fuel since hydrogen-air mixtures are highly reactive, thus hydrocarbons, able to form hydrogen through partial oxidation (reaction 4), are most commonly used in the gas mixture.



As there is no difference in the gas composition at each side of the cell, single chamber operation principle is based on the difference of electrodes catalytic activity towards hydrocarbon oxidation. When no current is drawn, the depletion of oxygen at the anode and the maximum concentration of oxygen at the cathode lead to an oxygen partial pressure gradient between both sides of the cell involving an open circuit voltage (OCV) creation.

The single chamber configuration has several advantages in comparison with conventional SOFCs: new cell geometries, stack assembly and cells miniaturization are more easily conceivable. These advantages open the way to new applications such as energy recovery and pollutant emission reduction. In such applications, cells might be embedded at the outlet of engine and could turn unburned hydrocarbons present in the exhaust gas into electricity allowing for instance the energy supplying of electronic devices in vehicles. More largely, such energy conversion device can address all applications where hydrocarbons are burnt such as stationary power plants where environmental and efficiency issues are identified.

To date, only a few authors have investigated such a system. Herman et al. [5] and Uchiyama [6] described equivalent devices in patents. Particularly, N. Uchiyama collaborated on testing such a system in real conditions with T. Hibino's group; two articles dealing with the results were published in 2008 [7,8]. Concerning the gas mixture used for tests, patents and articles expose only evasive or simplified compositions. Herman's patent [5] describes a mixture composed of hydrocarbons (e.g. methane, ethane ...), hydrogen and oxygen without any accurate composition. In Uchiyama's work [6], the studied atmosphere is composed of hydrocarbons, carbon oxides and air without any further details. The only work reporting the concentration of studied stream for single cell test was published by Hibino's group [7,8]. A mixture of four hydrocarbons (methane, ethane, propane and butane) with 1000 ppm of each hydrocarbon specie and with oxygen ranging from 1250 to 15,000 ppm is reported. For an electrolyte supported Ni–Ce_{0.8}Sm_{0.2}O_{1.9} (SDC)/8%Y₂O₃–ZrO₂ (YSZ)/La_{0.8}Sr_{0.2}MnO₃ (LSM) single cell, an open circuit voltage and a maximum power density respectively 1100 mV and 20 mW cm⁻² were measured at 800 °C, a temperature not really considered as realistic for the aimed application. Then, an output power of 1.2 W was delivered by a twelve-cells stack embedded at the exit of a scooter engine, which is still not high enough to provide energy to electronic devices included in a vehicle but proves the feasibility of such energy recovery system. Nevertheless, no exact composition of exhaust gas is given for the stack test at the exit of the scooter.

In the present work, further improvements including gas mixture composition, architecture of the cell and materials are initiated. Indeed, the selected gas mixture is based on a more realistic composition of exhaust gas flowing inside the catalytic converter of a thermal engine. The influence of oxygen content is investigated on the performances of cells. Anode supported architecture is selected instead of the usual electrolyte supported since it has proven an ability to deliver higher power densities by a lower resistance of thinner electrolyte [9]. For the cell components, most performing materials are selected. Ce_{0.9}Gd_{0.1}O_{1.95} (CGO) is used as

the electrolyte material due to a high ionic conductivity at intermediate temperature range: 0.025 S cm⁻¹ at 600 °C [10]. The anode is a typical cermet composed of nickel and electrolyte material. Two cathode materials are compared regarding the application, La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF), a well-known cathode material [11,12] and Pr₂NiO_{4+δ} (PNO) only used up to now for conventional SOFCs [13]. Finally, electrolyte microstructure is improved in order to enhance performances.

2. Experimental

2.1. Exhaust stream composition

The gas mixture used in this project is based on data provided by an engine manufacturer corresponding to the gas composition after the catalytic converter. However, it has been slightly modified to fit to laboratory conditions. The gas stream is hence composed of hydrocarbons (HC): 1/3 propane and 2/3 propene, and oxygen but hydrocarbons oxidation products are added: hydrogen, carbon monoxide, water and carbon dioxide; and finally nitrogen is used as balance gas. Three compositions are employed presenting different ratios *R* (HC/O₂): *R* = 0.21 corresponding to oxygen content required for total oxidation, *R* = 0.67 corresponding to partial oxidation and *R* = 0.44, an intermediate value. The compositions are reported in Table 1. The experiments were done at atmospheric pressure, so the oxygen partial pressure is ranging from 1.3 mbar (corresponding to *R* = 0.67) to 4.7 mbar (corresponding to *R* = 0.21). It is also noteworthy that there is more than 90% of nitrogen in the composition meaning that the mixture contains very low levels of reactive species.

2.2. Materials and cells preparation

All raw materials used for electrochemical tests and cells manufacturing are commercial powders. Suppliers and powder specifications are given in Table 2.

Anode supported cells are prepared by screen printing the electrolyte on the green anode made by tape casting. The slurry for tape casting is prepared according to the formulation previously described in the literature [14]. The powders mixture used in this paper is composed of 60 wt% of NiO from Novamet and 40 wt% of CGO from Rhodia. Electrolyte ink is composed of 70 wt% of CGO from Fuel Cell Materials and 30 wt% of a solvent-binder mixture (terpineol mixed with 5 wt% of ethyl cellulose). Various thicknesses of electrolyte are prepared by screen printing with respectively 3, 5 or 7 layers. The half cells are then co-sintered in two main steps. At first, a slow heating rate (60 °C h⁻¹) is performed up to 600 °C with a 1 h-dwell time to remove the binders contained in the anode tape. Then, a faster heating rate towards 1400 °C and a 6 h-dwell time are respected to sinter the half cells. The reduction of the anode is carried out at 650 °C for 4 h in a 6% H₂ atmosphere. Two cathode layers are then screen-printed on the reduced half-cell using an ink composed of 70 wt% cathode material and 30 wt% CGO (Fuel Cell Materials) as solid content. A first heating at 300 °C for 30 min in air is done to remove cathode ink binder and then cathode are annealed at 1100 °C in argon to avoid any anode reoxidation. A gold mesh is screen printed on top of the cathode to collect correctly the current during the experiment. Same heating treatment in air (300 °C, 30 min) as for the cathode is carried out and the gold mesh is finally annealed at 900 °C for 2 h under argon.

2.3. Fuel cells characterization

In SC-SOFC system, the geometry of the cell but also of the whole test chamber have a great influence on performances. That's

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