Experimental and model analysis of the co-oxidative behavior of syngas feed in an Intermediate Temperature Solid Oxide Fuel Cell

A. Donazzi [a, *], M. Rahmanipour [a], M. Maestri [a], G. Groppi [a], L. Bardini [b], A. Pappacena [b], M. Boaro [b]

[a] Dipartimento di Energia, Politecnico di Milano, Via Lambruschini 4, 20156, Milano, Italy
[b] Dipartimento di Chimica Fisica e Ambiente, Università degli Studi di Udine, Via Cotonificio 108, 33100, Udine, Italy

HIGHLIGHTS

- Ni-free, Ce-based IT-SOFCs are tested with syngas and biogas at 600 and 650 °C.
- The electro-oxidations of CO and of H_2 are active in parallel and contemporarily.
- A 1D, dynamic, heterogeneous and physically-sound MEA model of the cell is applied.
- The polarization curves and the EIS spectra are simulated based with the model.
- Power law rate equations are derived for the electro-oxidation of H_2 and of CO.

GRAPHICAL ABSTRACT
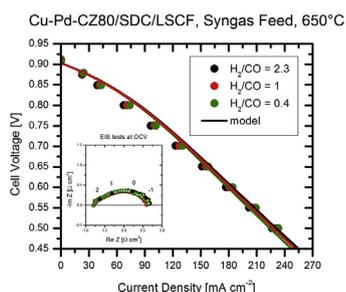
ARTICLE INFO

ABSTRACT

By means of model analysis, we show that, in the presence of syngas, the electro-oxidation of H_2 and that of CO occur in parallel and contemporarily on Samaria-doped Ceria ($Sm_{0.2}Ce_{0.8}O_{1.9}$, SDC) Intermediate Temperature Solid Oxide Fuel Cells (IT-SOFCs). The activation of a co-oxidative route is a most distinguishing feature of Ce-based cells, compared to traditional SOFCs. SDC electrolyte supported IT-SOFCs with Cu–Pd-CZ80 composite anodes and LSCF cathodes were tested under a wide range of operating conditions. Polarization and EIS measurements were collected at 600 °C and 650 °C with syngas mixtures ($2.3-0.4 H_2$/CO ratio), H_2/N_2 mixtures (from 97 to 30% H_2 v/v) and CO/CO_2 mixtures (from 97 to 50% CO v/v). A 1D, dynamic and heterogeneous model of the cell was applied to analyze the polarization and the EIS curves. The kinetics of the reactions of H_2 electro-oxidation, CO electro-oxidation and O_2 reduction were individually investigated and global power law rates were derived. The syngas experiments were simulated on a fully predictive basis and no parameter adjustment, confirming that the polarization behavior could be best reproduced exclusively by assuming the presence of the co-oxidative route. The IT-SOFCs were also exposed to biogas mixtures, revealing that the dry-reforming reaction was active.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Fuel flexibility is one of the most important advantages of Solid Oxide Fuel Cells compared to other types of fuel cells. In order to

* Corresponding author.
  E-mail address: alessandro.donazzi@polimi.it (A. Donazzi).

reduce the device volume and to intensify the power density, applications based on SOFCs for the distributed production of energy require the cell to operate with both traditional hydrocarbon fuels (CH_4 and LPG) and biomass derived fuels (biogas, ethanol). Several benefits in terms of cell lifetime and thermo-mechanical resistance are achieved by decreasing the operating temperature to 500—700 °C, leading to Intermediate Temperature SOFCs (IT-SOFCs) [1]. Lower temperatures ask for electrolytes different from YSZ, such as Samaria-doped Ceria (SDC) and Gadolinia-doped Ceria (GDC). The adoption of these electrolytes activates an internal short circuit current due to the partial reduction of the Ce^{4+}/Ce^{3+} couple, which lowers the cell performance and asks for the introduction of insulating barriers (e.g. ScSZ) in case of applicative purposes [2,3]. Novel materials are also required for the anode and the cathode, due to compatibility issues (formation of secondary phases, interdiffusion, delamination) and thanks to the possibility of optimizing the composition in order to increase the low temperature activity. Along with this, double-layered perovskite oxides are state of the art cathodes for IT-SOFCs [4]. With reference to the anode, Cu-based and Ce-based compounds have been widely explored in the literature. The addition of Cu is known to strongly inhibit the production of coke, even in the presence of dry methane feed, and to provide the necessary electronic conductivity to the electrode [5,6]. Ceria is exploited for its oxygen ion transfer capability, which makes it a very effective oxidation catalyst and allows to increase the volume active for the electro-oxidation, deepening the penetration distance of the C-removing oxygen ions and keeping the surface clean from coke [7]. Addition of noble metals (Pd, Rh or Pt) at dopant levels has been proved to boost the activity of Ce-based anodes, especially in the presence of methane and biogas, thanks to the increase in the reforming chemistry [8,9].

The adoption of novel composite materials triggers different catalytic and electrocatalytic routes compared to traditional Ni-based anodes, especially those processes related to the conversion of syngas and hydrocarbons. In light of this, it is generally understood that negligible direct electro-oxidation occurs when light hydrocarbons are supplied to the cell. Instead, the fuel is primarily reformed or partially oxidized to H_2 and CO rich mixtures (syngas). A question of interest is how H_2 and CO undergo the electro-oxidation process when they are mixed together in the anode: whether or not the oxidation of H_2 prevails on that of CO, or if a co-oxidation is feasible. Additionally, the oxidation of syngas leads to the production of CO_2 and H_2O, whose counter diffusion further enhances the steam reforming and the dry reforming catalytic chemistry, as well as the Water Gas Shift (WGS) equilibrium. These heterogeneous processes can possibly contribute to the balance between the electro-oxidation of H_2 and CO. Several efforts have therefore been devoted to unravel the mechanism of the electro-oxidative processes, in order to optimize the electrode design. In a comprehensive review, Gohniem and coworkers [10] have recently addressed the chemistry of the electro-oxidation of H_2 and CO, both individually and in the case of syngas mixtures: in Ni-YSZ anodes, the electrochemical conversion of syngas is governed by the H_2 electro-oxidation, with the WGS reaction being responsible for the conversion of CO to H_2O and H_2, for further electrochemical consumption. H_2 is the dominant electroactive species, whereas CO is not directly electro-oxidized: since the H_2 electro-oxidation kinetics are much faster than the electro-oxidation kinetics of CO (up to one order of magnitude), H_2 remains the favored electroactive species even when the excess of CO is significant [11]. Ultimately, the reason for this lies in the spillover and surface diffusion rates of H, which are much faster than those of CO, and allow for an easier transfer of H from the Ni metal site to the YSZ surface (where O^{2-} ions are provided). Much less investigation on this subject is reported for Ce-based anodes. Notably, however,

when using Cu—CeO_2-YSZ anodes in the presence of syngas mixtures, Costa-Nunes et al. [12] found that Ceria was active for both the electrochemical oxidation of H_2 and CO, contemporarily. That is, no predominance of the H_2 electro-oxidation was found, differently from Ni-YSZ anodes: possibly, this behavior could be attributed to the specific roles of Ceria and Cu, wherein the metal is almost inert and the spillover and diffusion reactions are blocked, while Ceria is active in both the oxidation of H_2 and CO.

Given the possibility of novel mechanistic routes, the research of materials must be closely accompanied by numerical model analysis to rationalize the chemical and physical phenomena occurring in the cell. Several electrochemical models are present in the literature, with different degrees of complexity with respect to both the approach and the kinetic schemes. Schemes ranging from detailed microkinetic mechanisms for the heterogeneous chemistry and the charge transfer chemistry [13—17] to Butler—Volmer frames with global power law rates [18,19] have been successfully applied. As well, different approaches have been validated, spanning from particle-level descriptions of the electrode microstructure [20,21] to mean-field descriptions that take into account average morphological parameters and average material properties [22]. Most of these models are devoted to traditional cells: in the case of novel material formulations, due to the lack of kinetic data and to the complexity of the electrodic compositions, physically-based membrane-electrode-assembly (MEA) models using global kinetic rates are well fitted and sufficiently informative.

In the present work, we show that the oxidation of CO and that of H_2 occur in parallel, and not in a mutual exclusive way, when syngas is fed to a Ce-based IT-SOFC. SDC electrolyte-supported IT-SOFCs with Cu—Pd-CZ80 composite anodes and LSCF cathodes were tested in the presence of syngas and biogas mixtures. Polarization and impedance measurements were carried out at 600 and 650 °C, over a wide range of gas compositions. A 1D, dynamic and heterogeneous model of the IT-SOFC, accounting for the presence of internal shorting currents and for the WGS chemistry, was applied to rationalize the behavior observed with syngas. The kinetics of the H_2 electro-oxidation and of the CO electro-oxidation were individually investigated with dedicated H_2/N_2 tests and CO/CO_2 tests. Power law kinetic equations were derived, which allowed to simulate the cell behavior in the presence of syngas. The comparison between model simulations and experimental measurements revealed that the best description could be achieved exclusively by assuming the presence of the co-oxidative route.

2. Experimental and theoretical tools

2.1. Materials and experimental methods

Electrolyte supported button cells (20 mm diameter, 0.82 cm^2 cathode area) were prepared and tested. The morphological

Table 1
Morphological properties of the cell.

Anode (Cu—Pd-CZ80)	
Thickness	150 μm
Porosity	0.4
Anode diameter	2 cm
Particle diameter	2 μm
Cathode (LSCF)	
Thickness	40 μm
Porosity	0.4
Cathode diameter	1.1 cm
Particle diameter	2 μm
Electrolyte (SDC)	
Thickness	380 μm