# Reversible operation of solid oxide cells under electrolysis and fuel cell modes: Experimental study and model validation

Domenico Ferrero *, Andrea Lanzini, Pierluigi Leone, Massimo Santarelli

*Department of Energy (DENERG), Politecnico di Torino, Corso Duca degli Abruzzi, 24, 10129 Turin, Italy*

## HIGHLIGHTS

- Performance of solid oxide cells is investigated with $H_2/H_2O$ and $CO/CO_2$ mixtures.
- Thermo-electrochemical model is developed for reversible solid oxide cells.
- Model validation is performed using experimental data.
- Physical consistency of activation parameters is verified.
- Evolutions of overpotentials and temperature within the cell are discussed.

## ARTICLE INFO

## ABSTRACT

A combined experimental and modeling study on reversible solid oxide cells (SOCs) is presented. Two commercial Ni/YSZ supported planar SOCs with the air electrode made by either LSM/YSZ or LSCF were characterized. The operation with $H_2/H_2O$ and $CO/CO_2$ gas mixtures was investigated by measuring current–voltage ($i$–$V$) curves and impedance spectra. An integrated thermo-electrochemical model for the simulation of $i$–$V$ characteristics of the reversible SOC is developed and calibrated on the experimental data. The model describes the electrochemical processes and mass transport of gaseous species at the electrodes and simulates the heat transfer within electrodes and electrolyte in the presence of distributed heat sinks/sources produced by electrochemical reactions and polarization overpotentials. Activation parameters of the electrodes evaluated from the model calibration are discussed and their physical consistency is verified with the support of the published literature. Activation parameters show a significantly higher activity for the LSCF electrode compared to the LSM/YSZ electrode in both fuel cell and electrolysis mode and higher activation resistances for the fuel electrode are observed in the operation with $CO/CO_2$ mixtures, due to the faster kinetics of $H_2/H_2O$ reactions. The proposed model is validated on current–voltage curves of the commercial cells tested with $H_2/H_2O$ mixtures, and the simulated evolutions of overpotentials and temperature within the cell are briefly discussed.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

The Europe 2020 strategy promotes the shift toward a resource-efficient, low-carbon economy based on renewable sources to achieve sustainable growth [1]. The move toward a renewable-based energy system will increase the share of intermittent electricity generation and the decentralization of the power system, promoting the growth of a diffused electricity storage infrastructure for grid balancing. Among the several electricity storage options, one of the most promising consists in the conversion of energy from the electrical into the chemical form by producing hydrogen through water electrolysis processes, in the framework of the 'power-to-gas' concept [2]. With power-to-gas, hydrogen is produced when the available electrical power exceeds the demand at off-peak times, stored in pressure or metal hydrides tanks, and then reutilized for electricity generation or fuels production [3].

Proton exchange membrane (PEM) and alkaline electrolyzers are the most widely applied electrolysis technologies in power-to-gas plants [4]. However, our previous work based on experimental evidences from lab tests has demonstrated that a SOC-based electrolysis option can widely compete with PEM, yielding even higher efficiency at high current densities, thanks to the advantages in thermodynamics and kinetic terms related to the temperature effects [5].

## List of symbols

| | |
|---|---|
| $B_0$ | permeability coefficient of the porous medium ($m^2$) |
| $D_{\alpha,\beta}^{eff}$ | effective molecular diffusion coefficient for a binary mixture of gases ($m^2\,s^{-1}$) |
| $D_{K,\alpha}^{eff}$ | effective Knudsen diffusion coefficient ($m^2\,s^{-1}$) |
| $E_{act}$ | activation energy ($J\,mol^{-1}$) |
| $F$ | Faraday constant ($C\,mol^{-1}$) |
| $h_{layer}$ | layer thickness ($\mu m$) |
| $k_{eff}$ | effective thermal conductivity ($W\,m^{-1}\,K^{-1}$) |
| $l_{air}$ | thickness of the air electrode ($\mu m$) |
| $l_{fuel}$ | thickness of the fuel electrode ($\mu m$) |
| $i$ | local current density ($A\,cm^{-2}$) |
| $i_0$ | exchange current density ($A\,cm^{-2}$) |
| $M_\alpha$ | molecular weight of the species $\alpha$ ($g\,mol^{-1}$) |
| $\dot{n}$ | molar flow rate ($mol\,s^{-1}$) |
| $p$ | total pressure in the electrode (Pa) |
| $\dot{Q}$ | heat source (W) |
| $q_s$ | volumetric heat source ($W\,m^{-3}$) |
| $R$ | ideal gas constant ($J\,mol^{-1}\,K^{-1}$) |
| $R_{Ohm}$ | Ohmic resistance ($\Omega\,cm^2$) |
| $\bar{r}$ | mean pore radius ($\mu m$) |
| $\bar{s}$ | molar entropy ($J\,mol^{-1}\,K^{-1}$) |
| $T$ | temperature (K) |

| | |
|---|---|
| $y$ | molar fraction (–) |
| $V_{cell}$ | cell voltage (V) |
| $V_{rev}$ | Nernst voltage (V) |
| $\alpha$ | charge transfer coefficient (–) |
| $\gamma$ | reaction coefficient (–) |
| $\gamma_{air}$ | kinetic activation parameter, air electrode ($A\,m^{-2}$) |
| $\gamma_{fuel}$ | kinetic activation parameter, fuel electrode ($A\,m^{-2}$) |
| $\Delta\bar{g}$ | Gibbs energy change ($J\,mol^{-1}$) |
| $\varepsilon$ | porosity (–) |
| $\eta_{act}$ | activation overpotential (V) |
| $\eta_{con}$ | conversion and diffusion overpotential (V) |
| $\eta_{Ohm}$ | Ohmic overpotential (V) |
| $(\rho c_p)_{eff}$ | effective volumetric heat capacity ($J\,m^{-3}\,K^{-1}$) |
| $\tau$ | tortuosity (–) |
| $\sigma_{\alpha\beta}$ | Lennard–Jones characteristic length (Å) |
| $\mu$ | fluid viscosity ($kg\,m^{-1}\,s^{-1}$) |
| $v$ | stoichiometric coefficient (–) |
| $\Phi$ | areic molar flow ($mol\,cm^{-2}\,s^{-1}$) |
| $\Omega_{\alpha\beta}$ | collision integral (–) |

Most of the power-to-gas plants providing hydrogen storage for electricity production rely on fuel cells, which allow to achieve higher efficiency than other conversion technologies while also maintaining high efficiency at partial load [2,6,7]. The use of reversible fuel cells that can operate in both electrolysis and fuel cell mode potentially allows the reduction of complexity, footprint and cost of the power-to-gas plant, unifying hydrogen production and utilization in the same device.

Given this framework, the present work is focused on reversible solid oxide cells (RSOCs). Several studies are investigating the performance of RSOCs and new materials for this type of applications are under development [8–15]. Although many validated models of solid oxide cells working either in fuel cell or electrolysis mode are available in the literature, few attempts have been made to model the reversible operation of SOCs and validate the models against experimental data. Models of tubular and microtubular RSOCs have been presented by Moyer et al. [16] and García-Camprubí et al. [17]; in these studies, the model results have been compared with experimental data obtained on fuel electrode supported Ni/YSZ–YSZ–LSM/YSZ cells tested in reversible mode. Ni et al. [18–20] developed a mathematical model for reversible solid oxide cells with oxygen ion- and proton-conducting electrolytes and compared the results with polarization curves obtained for SOCs tested separately in fuel-cell or electrolysis mode. Njodzefon et al. [21] presented a 0D isothermal model validated on a reversible Ni/YSZ–YSZ–GDC–LSCF square button cell, while Jin et al. [22] has reported the results of a 2D model compared with $i$–$V$ curves obtained for a Ni/YSZ–YSZ–LSM circular button cell. Kazempoor et al. [23] calibrated and validated an RSOC model on the current–voltage curves of a fuel electrode supported Ni/YSZ–YSZ–LSM/YSZ square cell with an active electrode area of $4 \times 4$ cm tested with $H_2/H_2O/CO/CO_2$ mixtures.

The purpose of this study is to develop and validate a model for the simulation of current–voltage ($i$–$V$) characteristics of planar RSOCs. For this purpose, the performance of commercial-size cells made with different air electrode materials (LSM/YSZ and LSCF) has been investigated and an integrated thermo-electrochemical model has been first calibrated and then validated on the experimental data.

The activation parameters evaluated from the model calibration show a significantly higher activity for the LSCF electrode compared to the LSM/YSZ one, in both fuel cell and electrolysis mode, and higher activation resistances for the fuel electrode are observed in the operation with $CO/CO_2$ mixtures, due to the faster kinetics of $H_2/H_2O$ reactions.

The proposed model successfully predicts the current–voltage characteristic of RSOCs tested with $H_2/H_2O$ mixtures, and the combined application of experiments and mathematical modeling provides an original approach to the investigation of electrode performance that has proven successful in describing the activation behavior of commercial electrodes.

## 2. Experimental

Two types of commercial planar circular-shaped fuel electrode-supported solid oxide cells were characterized (H.C. Starck, Germany). The cells have a diameter of 80 mm with an active surface area of ~47 cm². The cells have identical fuel electrode and electrolyte with a different air electrode. Fuel electrodes consist of a porous 5–10 μm thick nickel/zirconia cermet (Ni/8YSZ) supported on a 450–550 μm thick Ni/8YSZ substrate, and the electrolytes of a 4–6 μm dense layer of 8YSZ. In one configuration, the air electrode consists of a porous double layer made by a 15–30 μm thick lanthanum strontium manganite/zirconia (LSM/8YSZ) composite with 15–30 μm of pure LSM current collector layer, in the other of a porous 30–60 μm thick lanthanum strontium cobalt ferrite (LSCF) layer with a 2–4 μm thick yttria doped ceria (YDC) blocking layer. Microstructural characteristics of the electrodes can be obtained by 3D reconstruction using FIB-SEM techniques [33,58]. In particular, the estimated volume fractions of the solid phases reported in the literature for typical Ni/YSZ, LSM/YSZ and LSCF electrodes range between 40–50% (Ni), 45–50% (LSM), and 50–60% (LSCF) [59].

For simplicity, the cell with LSCF air electrode is referred to as "cell A" while the one with the LSM/YSZ air electrode is "cell B" in the following of this work.

Experiments were performed in a temperature-controlled oven. Cells were placed in an unsealed alumina ($Al_2O_3$) housing