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A numerical and experimental comparison of a single reversible molten carbonate cell operating in fuel cell mode and electrolysis mode

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HIGHLIGHTS

- A single Molten Carbonate Cell is operated in reversible mode.
- Zero-dimensional MCFC fitted model tested in molten carbonate electrolysis cell.
- Experimental and numerical comparison of reversible molten carbonate cell performance.
- Hydrogen and syngas production by Molten Carbonate Electrolysis Cell.
- Degradation in reversible molten carbonate cell.

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ABSTRACT

This work summarizes the experimental and numerical activities done in a molten carbonate cell operated in reversible mode using a single cell with an electrodes-electrolyte interface area of 80 cm^2. The experimental activity is divided into two sets. Firstly, running the cell only in fuel cell mode in order to compare five electrochemical zero-dimensional models available in literature and choose the one with the smallest deviation with respect to the experimental data, which is applied later in electrolysis mode. The second experimental set is focused on studying the cell working in reversible mode by varying the gas composition entering the fuel electrode and oxygen electrode, the ratio of the flow rate of the oxygen electrode to the fuel electrode and the cell temperature. The results indicate that molten carbonate cells present lower polarization losses in electrolysis mode than in fuel cell mode. According to the parameter variations, a lower cell temperature decreases the performance in both modes; besides, in the fuel electrode the results indicate carbon dioxide reduction apart from the reduction of water; moreover, the oxygen electrode is strongly sensible to the high presence of carbon dioxide that could cause a faster nickel oxide dissolution accelerating the degradation. Throughout the experimental campaign the molten carbonate cell presents a quite high degradation, contrary to previous results of reversible molten carbonate cells carried out using button cells where an improvement was found instead of a degradation. Electrolyte refilling was tried at the end of the second experimental campaign obtaining a significant decrease of internal resistance with a difference of only 20.6% with respect to the initial condition. According to the experimental activity, the fitted model gives a good prediction of the performance in fuel cell mode; however, in electrolysis mode the prediction is weak mainly attributed to the differences in the diffusive phenomena between both operative modes.

1. Introduction

Our planet is going through important alterations caused by the great increase in greenhouse gas (GHG) emissions produced by the excessive use of fossil fuels to maintain our current lifestyle. Carbon dioxide (CO_2) represents about 95% of the energy-related emissions, and around 80% of global anthropogenic GHG emissions [1]. CO_2 concentration has been increasing compared to the rather steady level of the pre-industrial era (about 280 ppm) up to concentrations of 406.7 ppm in 2017 [1,2]. Facing this problem, some approaches for limiting climate change include: enhance energy efficiency, use of renewable energies, decrease deforestation and reduce industrial and

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Nomenclature

A	constants for model 1 equations
F	Faraday constant, 96,485 C/mol
G	Gibbs free energy, kJ/K
h	specific enthalpy, kJ/kmol
I	current, A
j	current density, mA/cm^2
$\dot{m}$	mass flow rate, kg/s
$\dot{n}$	molar flow rate, kmol/s
p	pressure, kPa
P	constant for model 5 equations
$\dot{Q}$	heat rate, W
R	specific electrical resistance, Ω cm^2
R	ideal gas constant, 8.314 kJ/kmol K
s	specific entropy, kJ/kg K
T	temperature, K
U	utilization factor
V	voltage, V
y	molar fraction

Subscripts

act	activation
conc	concentration
e	exit
fe	fuel electrode
in	inlet
L	limiting point
m	model
oe	oxygen electrode
ohm	ohmic losses
r	reacting
ref	reference condition, 25 °C

agricultural emissions; and compensate the continuous CO_2 emissions by the development and implementation of carbon dioxide removal technologies [3].

Renewable energies (e.g. wind) have the characteristic to be intermittent because they are dependent on weather conditions. This makes integration with current power networks a challenge in terms of matching fuel/energy source, generation, transmission, distribution and customer-side requirements. To cover these requirements some Energy Storage Systems (ESS) have been proposed, which include pumped hydro storage, compressed-air storage, battery energy storage, superconducting magnetic energy storage, thermal energy storage and chemical energy storage technologies [4]. A review of the different energy storage technologies and information on the real life applications, their differences and unique features helping in the determination of the best energy storage technology are given by Aneke and Wang [4].

Concerning chemical energy storage technology, fuel cells working in electrolysis mode play an important role because they can be integrated in a Power-to-Gas (PtG) system to convert surplus electricity coming from a renewable source into gaseous energy carriers, mainly hydrogen and methane that can be transformed back into electricity [5]. Robinius et al. [6] analyze the potential use of a PtG system using an alkaline electrolyzer in the electrical distribution grid as an alternative to a network expansion with cables, focusing on determining the size of the electrolyzer to cover a specific demand, the effect on the voltage grid by the installation of the electrolyzer and the economic feasibility of the system. The results indicate that laying a cable represents around 30% of the investment and the rest, the electrolyzer cost. In the case that a PtG system is dedicated mainly to the production of hydrogen, this should meet the requirements of the potential consumers. The pressure level and the purity of hydrogen are substantial elements to achieve this goal, where auxiliary equipment is needed to increase the pressure of the gases and clean the hydrogen to desired levels. Bensmann et al. [7] study numerically two configurations of a PtG using a Proton Exchange Membrane (PEM) electrolyzer unit with auxiliary devices including a multistage compressor, two cooler units and a dryer unit. The hydrogen delivery pressure analyzed was between 1 and 100 bar, presenting the energy demand by process in dependence of electrolyzer pressure for different delivery pressure. The results show that the energy demand for drying dominates the total energy balance at low delivery pressure, besides higher electrolyzer pressures increase the losses due to hydrogen crossover.

PtG is a promising technology, nevertheless it has many system variations, and their environmental performances need to be evaluated and compared with conventional technologies. Zhang et al. [8] investigate the environmental performance of a PtG system using Life Cycle Assessment (LCA) covering aspects including supply of electricity, product gases (hydrogen and methane), the use of CO_2 Capture and Utilization (CCU) obtained by different sources, the comparison with conventional technologies, and the investigation of further environmental impacts of PtG in addition to the impact of global warming potential. The analysis varies the used electrolyzer considering an alkaline electrolyzer and a PEM electrolyzer. The results of system variations show that PtG can, depending on electricity supply and CO_2 source, reduce GHG emission compared to conventional gas production technologies.

Among electrolyzers, the most mature and commercial is the Alkaline electrolyzer [9,10], followed by the Proton Exchange Membrane (PEM) electrolyzer [9]. The capital costs for alkaline and PEM electrolyzer systems are presented in [6,11]. Solid Oxide Electrolyzers (SOECs) are in laboratory stage, however they have been greatly advanced in the last years related to experimental and numerical aspects. Menon et al. [12] carried out a parametric analysis of the principal variables affecting the performance of a SOEC using a quasi-two-dimensional model. The thermoneutral voltage has been found using an isothermal analysis. This result is important in order to maximize efficiencies, via conscious choice of optimum design for steam electrolysis systems. Klotz et al. [13] use a zero-dimensional model, previously developed by Leonide et al. [14] to predict the performance of Solid Oxide Fuel Cells (SOFC), to simulate the behavior of small and large area cells in SOFC and SOEC mode. Ferrero et al. [15] studied experimentally and numerically reversible solid oxide cells. Two commercial Ni/YSZ supported planar solid oxide cells with the air electrode made by either LSM/YSZ or LSCF were characterized. The numerical model was divided into two parts: the first one characterizes the electrochemical process and mass transport of gaseous species at the electrodes, the second one takes results from the previous calculations to determine the heat transfer in the system. Kazempoor and Braun [16] performed a parametric analysis to investigate the effect of various operating parameters related to SOEC electrochemical performance, as well as hydrogen and syngas production. Some of the results indicate that carbon dioxide plays an important role increasing the electrochemical losses at higher CO_2 concentrations. Luo et al. [17] carried out an exergy analysis to compare three methane production systems including (1) water electrolysis + Sabatier reactor, (2) water/carbon dioxide co-electrolysis + methanation reactor (MR), and (3) a single SOEC-MR. Moreover, a comparison of SOEC, proton exchange membrane electrolysis cell and an alkaline electrolysis cell is performed. The results obtained shows that SOEC presents a higher efficiency. Besides, according to the methane production systems the single SOEC-MR presents the highest efficiency. Mehran et al. [18] tested a fabricated