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Molten Carbonate Fuel Cell performance analysis varying cathode operating conditions for carbon capture applications

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HIGHLIGHTS

- MCFCs as CO_2 concentrators is a promising route for carbon capture.
- MCFCs capture CO_2 by feeding the cathode with exhaust gases from a CO_2 source.
- Different mixtures are considered in cathodic feeding as well as time variation.
- A correlation is found among operative parameters and single EIS equivalent circuit coefficients.
- EIS provides a performance monitoring methodology to be applied to MCFC in CCS configuration.

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ABSTRACT

The results of a systematic experimental campaign to verify the impact of real operating conditions on the performance of a complete Molten Carbonate Fuel Cell (MCFC) are presented.

In particular, the effects of ageing and composition of water, oxygen and carbon dioxide in the cathodic feeding stream are studied through the analysis of current-voltage curves and Electrochemical Impedance Spectroscopy (EIS).

Based on a proposed equivalent electrical circuit model and a fitting procedure, a correlation is found among specific operating parameters and single EIS coefficients. The obtained results suggest a new performance monitoring approach to be applied to MCFC for diagnostic purpose.

Particular attention is devoted to operating conditions characteristic of MCFC application as CO_2 concentrators, which, by feeding the cathode with exhaust gases, is a promising route for efficient and cheap carbon capture.

1. Introduction

In the last few years, the growing concerns about global warming have strongly encouraged innovative carbon capture solutions to decrease CO_2 emissions. Several studies have shown how critical topics, such as the increasing energy demand and the related issues concerning environmental sustainability and energy efficiency, could find an answer with promising solutions. The application of Molten Carbonate Fuel Cell (MCFC) technology [1–4] to Carbon Capture and Storage (CCS) or Carbon Capture and Utilization (CCU) represents one of these.

MCFCs are one of the most efficient power generators for direct energy conversion, characterized by wide operating flexibility. In addition, this technology can be exploited as CO_2 concentrator thanks to its intrinsic operating mechanism. In fact, the electrochemical reactions that take place within the MCFC involve the migration of the CO_2 from the cathode inlet to the anode outlet. During this process, the MCFC can work as power generator and, simultaneously, as CO_2 separator from an exhaust gaseous stream which can be fed to the cathode.

See Barelli et al. [5] for a detailed description of a simplified scheme of the MCFC operation as CO_2 concentrators, when installed downstream a thermoelectric plant or a combustion device included in a different industrial process. Further descriptions of similar system are described, for example, in Campanari et al. [6] or Caprile et al. [7].

This MCFC configuration was investigated in several previous

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Nomenclature

ASR	Area Specific Resistance
CCS	Carbon Capture and Storage
CCU	Carbon Capture and Utilization
CPE	Constant Phase Element
D	Diffusion coefficient
DRT	Distributed Relaxation Times
EIS	Electrochemical Impedance Spectroscopy
IV	Current Density-Voltage curve
L	Effective diffusion thickness
MCFC	Molten Carbonate Fuel Cell
OCV	Open Circuit Voltage
p	Pressure
P_k	Partial pressure of the species κ
P_i	i = 1, …, 8; empirical coefficients for the kinetic model
Ri	I = 1, 2, 3; empirical coefficients for resistances of the equivalent circuit
R_{TOT}	Overall cell resistance, Ω cm^2
R_W	Resistive component of the Warburg impedance
T	Temperature, K
W	Warburg Element
WGS	Water Gas Shift reaction
y_k	Molar fraction of species κ
Z_{Im}	Imaginary part of impedance
Z_{Re}	Real part of impedance
Z_W	Generalized finite-length Warburg impedance
ΔP_{max}	Variation of the maximum power produced
ϑ	Fraction of the water vapour fed at the cathode side in the bulk that reacts with CO_2
Ψ	Diffusion Thickness
Φ	Free coefficient for the generalized finite-length Warburg impedance

works, involving both experimental [8–11] and modelling [6,12–21] activities as well as correlated topics as the fuel/oxidant pollution problems [18,22–24] and the material performance optimization [25,26].

MCFCs are flexible from the point of view of the fuel which can be used [27], but also allows the use of a wide range of mixture compositions as oxidant.

The basic conditions required for the cathodic feeding are a CO_2 concentration above 5% and a partial pressure ratio P_{O_2}/P_{CO_2} higher than 0.5 for low O_2 content (<4–5%) [10].

Usually these constraints can be respected in CCS or CCU applications and MCFC can be used to concentrate CO_2 from various sources: from power production (e.g. based on reciprocating internal combustion engines, combined cycles or coal plants [28]) to industrial processes (21% of 2013 greenhouse gas emissions associated with human activities in U.S. can be ascribed mainly to cement, iron and steel production [29]).

Nevertheless, similar applications can involve operating conditions near to critical working points, for example due to a low CO_2 content, so that the monitoring of performance and degradation results particularly important. Nevertheless, similar applications can involve MCFC working close to the bounds of its operating domain, for example when the treated exhaust gas has a low CO_2 content. In these cases, it is fundamental to monitor the MCFC performance and degradation. In addition, the effect of the presence of water at the cathode side, expected in CCS, CCU and in general other industrial applications, is another topic to be deeply investigated.

In this scenario, Electrochemical Impedance Spectroscopy (EIS) is proposed as a powerful tool to assess the MCFC performance. EIS analysis allows the isolation effects of the electrochemical reactions occurring in the cell and allows the identification of the corresponding basic operating parameters, following the pioneering works of Selman et al. [30] or Nishina et al. [31]. This technique is under continuous development and improvement, for example the novel approach to the EIS interpretation through the distributed relaxation times (DRT) method is very promising [32,33].

In literature, many works exploit EIS interpretation for in-depth electrochemical analysis. These works are usually limited to materials characterization [34,35] by operating on simplified fuel cell systems (i.e. button cell or half-cell), in safe or particular (to point out specific aspects) conditions [36], far from the realistic operative ones.

Rough assessments of MCFC performances, operated specifically in CCS or CCU configuration and in real working conditions, were performed by several authors [11,37–39]. Nevertheless, a systematic discussion is not conducted and the experimental results are not analytically correlated to the imposed operating conditions.

The main aim of the present study is to analyse the correlation between the EIS data and the variation of relevant operating parameters on a complete MCFC tested in real working conditions characteristic of a CCS or CCU configuration. In addition, particular attention is devoted to the effect of the water presence at the cathode side.

Each investigated operating point, defined by a specific cathodic mixture and ageing, is characterized through current density-voltage (IV) curve and EIS analysis.

To provide a systematic mapping of the MCFC performance, the cathodic mixture is varied by modifying the relative content (in terms of molar fraction) of the O_2, CO_2, and H_2O species, keeping constant the overall flow by balancing with nitrogen, as inert inside the cell. As a result, the IV and the EIS parameters inferred from the experimental campaign are fully characterized enabling their proper correlation to the variation of a specific operating parameter. The obtained IV curves and EIS spectra are presented and discussed in the present paper.

These results, based on the experimental evidence of a complete cell, have an impact opening routes to monitor the MCFCs performances for diagnostic purpose. Indeed, EIS is a well attested method as diagnostic tool in the fuel cells dedicated literature [40,41], mainly for solid oxide fuel cells (e.g. Refs. [42–44]) and MCFC field [36,45,46]. The present work adopts this philosophy, usually applied to fuel cell degradation monitoring, and extends it to the monitoring of the fuel cell performance due to the change of working points (i.e. the particular cathodic mixture), distinguishing the impedance spectrum variations due to degradation and operating conditions.

In particular, an equivalent electrical circuit is proposed and the dependence of its main components on the operating conditions is highlighted, suggesting an empirical correlation from these results and the main phenomena affecting MCFC performance.

The work, related to a reference behaviour and its deviation, constitutes a basis for future investigations for developing a dedicated diagnostic tool.