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A reduced order model of Molten Carbonate Fuel Cell: A proposal

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ABSTRACT

The mathematical model of the Molten Carbonate Fuel Cell (MCFC) is presented. The new approach for modeling the voltage of MCFC is proposed. Electrochemical, thermal, electrical and flow parameters are collected in the 0-D mathematical model. The aim was to combine all cell working conditions in as a low number of factors as possible and to have the factors relatively easy to determine. A validation process for various experimental data was made and adequate results are shown. The presented model was validated for various fuel mixtures in relatively wide ranges of parameters. A distinction is made between the "design-point" and "off-design operation".

1. Introduction

Fuel cells, especially high temperature (Molten Carbonate Fuel Cell—MCFC and Solid Oxide Fuel Cell—SOFC) are very promising technologies with still growing research and development activities [1–6]. MCFCs are potential sources of energy due to their high efficiency and possibilities of direct use of hydrocarbons. Moreover, their high working temperature allows for the possibility of using lower cost catalysts (Ni vs. Pt) and possibility of adding a gas turbine subsystem to increase total efficiency [7]. Additionally, MCFC can be used for CO_2 separation from fossil fuel power plants [8,9] what makes this technology very promising in comparison to other techniques [10].

There are many mathematical models of the single molten carbonate oxide fuel cell (MCFC) [11–35]. MCFC performance modeling is related to the multi-physic processes taking place on the fuel cell surfaces. Heat transfer together with electrochemical reactions, mass, and charge transport are conducted inside the cell. The MCFC models found in the literature are based mainly on mathematical descriptions of these physical, chemical, and electrochemical properties.

There are many parameters which impact cell working conditions, e.g. electrolyte material, electrolyte matrix thickness, cell temperature, inlet and outlet gas compositions at anode and cathode, anode and cathode porosities etc. The MCFC models developed thus far are mainly based on the Nernst equation, activation, ohmic, and concentration losses or anode, electrolyte and cathode losses. This in effect means that a given current–voltage curve is approximated by several factors such as current limiting and exchange current among others.

Generally speaking, two approaches are used for MCFC mathematical modeling. It should be noted that both equations are probably corresponded to the same model, only the summation terms are grouped in a different way:

$$E_{MCFC} = E_{OCV} - \eta_{anode} - \eta_{electrolyte} - \eta_{cathode} \quad (1)$$

and

$$E_{MCFC} = E_{max} - \eta_{act} - \eta_{\Omega} - \eta_{con} \quad (2)$$

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Nomenclature

α	transfer coefficient
ΔH_{c1}, ΔH_{c2}, ΔH_{c3}	activation energy of cathode resistance
δ	thickness, cm
$\dot{n}$	molar flow, mol/s
η	voltage losses, V
η_f	fuel utilization factor
max	maximum
Ω	Ohmic
σ	conductivity, S/cm
A	frequency factor of anode/cathode/internal resistance
A	fuel cell area, cm^2
a, b, c	empirical coefficients
A_a	a factor
A_{c1}, A_{c2}, A_{c3}	frequency factors of cathode resistance
act	activation
C_1, C_2	coefficients calculated by using experimental data
C_a	parameter related to anode
con	concentration
E	voltage, V
eq	equivalent
F	Faraday's constant
i_0	exchange current density, A/cm^2
i_1	internal ionic current density, A/cm^2
i_2	internal electric current density, A/cm^2
i_3	external electric current density, A/cm^2
i_l	limiting current density, A/cm^2
i_{max}	maximum current density, A/cm^2
j	cell layer number
n	total number of cell layers
OCV	Open Circuit Voltage
p	partial pressure, Pa
Q	empirical coefficient
R	universal gas constant
r_1	area specific internal ionic resistance, cm^2/S
r_2	area specific internal electric resistance, cm^2/S
R_c	cathode polarization
T	absolute temperature, K

Most of the equations require the addition of numerous factors (porosity, tortuosity, ionic and electronic paths, etc.) that are difficult to determine and which are often related to the microscopic properties of the cell which govern both the chemical and electrochemical reaction. Very often those parameters are used as the fitting parameters with very questionable physical background—"*Actually, D is not yet used as its physical value. It is rather fitted so that physically realistic results are obtained. (…) Other parameters are then incorporated into the fitted D, an «effective diffusion coefficient»*" [36].

As the examples the following factors are very often used just as the fitting parameters [37]:

- internal resistance (e.g. a, b, c, Q, A) [23,29,38,39]
- anode overpotential (anode losses) (e.g. A_a, C_a) [27,38]
- cathode overpotential (cathode losses) (e.g. R_c, A_{c1}, A_{c2}, A_{c3}, ΔH_{c1}, ΔH_{c2}, ΔH_{c3}, C_1, C_2) [27,38,40]
- activation losses (η_{act}) (e.g. i_0, α) [29]
- concentration losses (η_{con}) (e.g. i_l) [29]

Those approaches result in relatively good agreement with particular experimental data (for which adequate factors—as listed above—were obtained) and poor agreement for the other cases—within the model parameters must be fitted once more time. A fitting approach is tightly connected to the physical properties and meaning of parameters is followed. It should be noted that "intelligent" fitting of model parameters is a very important aspect of successful model development. On the other hand, the fitting procedure can take longer time that the utilization of model itself.

This is particularly relevant in the case of complex fuels feeding, where it is not easy to determine all necessary coefficients and factors even for a few current–voltage curves generated with dry hydrogen as a fuel. The addition of other compounds (CH_4, CO, etc.) makes this task much more difficult. The models developed to date have been based on deep analysis of fundamental processes which occur on the fuel cell surfaces. This approach is very important for understanding the main processes behind the working principles of the fuel cell. On the other hand, the fuel cell is simply one element in a complex system. The choice of optimum system configuration is also important, and an extremely detailed model, which includes many electrochemical factors fitted to the experimental data, is of limited use with respect to system optimization. Occasionally, high complexity models are integrated and used in system-wide studies [30,41]. The optimizing processes and design point selections require a different approach when the size of the cell surfaces and the working parameters of the cell affect other system elements. Optimization of the system often means changes in the operation conditions of the fuel cell.

A new model is proposed and the governing equations of this model are presented in this paper. The presented model was used for specific purposes:

- estimating possible utilization of a MCFC for reducing CO_2 emission [42–45],
- investigating and developing a possible control strategy for MCFC-GT hybrid system [44],

which clearly shows the comprehensive nature of the model. In this paper a much deeper analysis of the model configuration is made to demonstrate its advantages and disadvantages. In response to numerous requests, a detailed description of the model is presented and a validation process based on experimental data is provided.

2. Theory

Mathematical modeling is now the basic method for analyzing fuel cells [46], most often a zero-dimensional approach is used for modeling the MCFC. Generally speaking, MCFC working principles are based on partial oxygen and carbon dioxide