Journal of Power Sources 330 (2016) 18–27

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Kinetic modelling of molten carbonate fuel cells: Effects of cathode water and electrode materials

E. Arato [a], E. Audasso [a, *], L. Barelli [b], B. Bosio [a], G. Discepoli [b]

[a] PERT, Department of Civil, Chemical and Environmental Engineering, University of Genova, Via Opera Pia 15, 16145 Genova, Italy
[b] Department of Engineering, University of Perugia, Via G. Duranti 67, 06125 Perugia, Italy

HIGHLIGHTS

- An updated kinetic formulation to described MCFC performance has been formulated.
- The effect due to H2O fed at the cathode side is considered.
- An easy way to adapt the formulation to MCFC working with different materials is presented.

ARTICLE INFO

Article history:
Received 1 July 2016
Received in revised form
25 August 2016
Accepted 29 August 2016
Available online 4 September 2016

Keywords:
Model
Kinetics
Water vapour
Parameter identification
Experimental analysis
Theoretical analysis

ABSTRACT

Through previous campaigns the authors developed a semi-empirical kinetic model to describe MCFC performance for industrial and laboratory simulation. Although effective in a wide range of operating conditions, the model was validated for specific electrode materials and dry feeding cathode compositions.

The new aim is to prove that with appropriate improvements it is possible to apply the model to MCFC provided by different suppliers and to new sets of reactant gases. Specifically, this paper describes the procedures to modify the model to switch among different materials and identify a new parameter taking into account the effects of cathode water vapour.

The new equation is integrated as the kinetic core within the SIMFC (SIMulation of Fuel Cells) code, an MCFC 3D model set up by the PERT group of the University of Genova, for reliability test. Validation is performed using data collected through tests carried out at the University of Perugia using single cells.

The results are discussed giving examples of the simulated performance with varying operating conditions. The final formulation average percentage error obtained for all the simulated cases with respect to experimental results is maintained around 1%, despite the difference between the basic and the new conditions and facilities.

1. Introduction

High temperature fuel cells (Molten Carbonate Fuel Cell – MCFC and Solid Oxide Fuel Cell – SOFC) are promising technologies with high efficiency that can be applied for energy production in integrated or more complex systems [1,2], and as a mean for carbon capture in CCS (Carbon Capture and Storage) applications [2–7].

Because of their possible uses, research on MCFC is currently conducted over different topics. The main research issues that characterize the current studies on MCFCs are the improvement and development of new electrode, matrix and electrolyte materials to enhance the overall performance [8–13] and resistance to pollutants [14–18]. Another not less important research topic concerns MCFC kinetics and system simulation. In fact, simulating a scientific problem can be an effective tool to gain a wider insight of it, needing reduced efforts in terms of both time and investments. This does not only favour further research activities, but also direct industrial application, for example helping in finding new technological solutions and in identifying optimal operating conditions. For these reasons, at present, many studies are conducted on many aspects of the MCFC technology. Regarding performance simulation, in Ref. [19] a reduced order model to describe the performance of MCFC with different anode (in H2 and CO_2) and cathode (in CO_2 and O_2) gas compositions was developed, while in Ref. [20],

* Corresponding author.
E-mail address: emilio.audasso@gmail.com (E. Audasso).

http://dx.doi.org/10.1016/j.jpowsour.2016.08.123
0378-7753/

combining momentum, energy, mass, charge balance and a kinetic equation, a model characterized by a dimensionless analysis is presented. Regarding MCFC degradation and performance losses [21], introduces a model whose aim is to describe the degradation of the cathode of MCFC, while [22] presents a simulation of the gas distribution inside the cell; in fact a maldistribution may result in efficiency loss both in stack and in single cell facilities. Another important aspect is the process control of which a model is presented in Ref. [23].

In previous works we proposed and developed a semi-empiric kinetic formulation, which insures a theoretical consistency as well as an empirical approach based on devoted experimental tests [24,25]. The final formulation was written considering the literature knowhow and introducing new features, aiming to allow an effective and easy validation by interested industries thanks to a minimum number of needed experimental tests.

The model obtained was integrated as the kinetic core in the SIMFC (SIMulation of Fuel Cells) code set up by the PERT group of the University of Genova, allowing the simulation of MCFC behaviour on the basis of local mass, energy, charge and momentum balances [26,27].

Even though the proposed kinetic formulation managed to reproduce the experimental performances with a small error (1.04% for the most recent work [24]) in a wide range of operating conditions, the model was based on specific working material, and therefore it cannot be applied as it is to every kind of MCFC test facilities.

In this paper, the procedure to modify the model in order to switch among different MCFC devices is described together with its experimental validation: this is an innovative approach since the models are usually developed for specific test facilities. Moreover, the effect of the water vapour on the kinetics, that is briefly analysed in literature [28,29], is here further investigated and added to the formulation. The final result is an effective MCFC model which allows a good predictive analysis on different MCFC technologies and in any operating application. Therefore, it can be proposed as the core of planning, control, optimising or diagnostic tools in the incoming context where MCFCs could have a new industrial role in the scenario of worldwide energy production.

2. Modelling background

The measurable voltage of a MCFC can be effectively expressed through the following equation:

$$\Delta V = \Delta E - R_{TOT} \cdot J \tag{1}$$

where ΔV is the measurable cell voltage, ΔE is the voltage at the thermodynamic equilibrium given by the Nernst equation, R_{TOT} is the overall cell resistance and J is the current density applied to the cell.

According to [24,25] the resistance term can be rewritten as:

$$\begin{aligned} R_{TOT} &= R_{Ohm} + R_{CAT,CO_2} + R_{CAT,O_2(CO_2)} + R_{AN,H_2} \\ &= \mathrm{P}_1 \exp\left(\frac{\mathrm{P}_2}{T}\right) + \frac{\mathrm{P}_3 T \exp\left(\frac{\mathrm{P}_4}{T}\right)}{p \ln\left(1 - 1.5\, y_{CO_2}\right)^{-1}} \\ &\quad + \frac{\mathrm{P}_5 T \exp\left(\frac{\mathrm{P}_6}{T}\right) p^{0.5} y_{CO_2} y_{O_2}^{0.5}}{\ln\left(1 - 3\, y_{O_2}\right)^{-1}} + \frac{\mathrm{P}_7 T \exp\left(\frac{\mathrm{P}_8}{T}\right)}{p \ln\left(1 + y_{H_2}\right)} \end{aligned} \tag{2}$$

Eq. (2) was deduced through kinetic and thermodynamic considerations that include.

1. The contribution due to the activation loss was neglected since, as experimental results confirm [30,31], its contribution to the overall loss is negligible.
2. The first term (R_{ohm}) is a simplified expression of the internal resistance [32].
3. The second (R_{CAT,CO_2}) and the third ($R_{CAT,O_2(CO_2)}$) addends represent the cathode polarization resistance that depends on CO_2 and O_2 partial pressures. In literature, two possible paths for the O_2 evolution are described [28,33]: the peroxide and the superoxide paths; in Eq. (2) the former was used as suggested by experimental tests [24,25]. In the third addend, the dependence on O_2 following the peroxide path is expressed, while in the second addend the dependence on CO_2. Also, as described in Ref. [24], the effect of the induced fluxes on the gas diffusion is considered.
4. The last term (R_{AN,H_2}) represents the anode polarization resistance. In particular, the dependence on the H_2 molar fraction was calculated taking into account the penalisation factor that affects the H_2 flux due to the counter-diffusion of the anodic products [25].
5. P_1, P_2, P_3, P_4, P_5, P_6, P_7, P_8 are empirical coefficients [15,24,30,34,35]. The P_i values included in the model are presented in Table 1.

Eq. (2) was tested in Ref. [24] by using different MCFC single cells provided by the KIST (Korea Institute of Science and Technology) and under various operating conditions, obtaining an average error of the fitting of about 1%.

In this work a similar approach was followed, but cells provided by another supplier and a wet cathode feeding were used, so a new evaluation of the occurring reactions and related kinetics parameters was performed.

3. New experimental campaign

The experimental campaign scheduled within the present work was conducted at the Fuel Cell Laboratory of the University of Perugia (Italy). The experimental data used in this paper were collected using a single cell apparatus. The cells, provided by FCES (*Fuel Cell Energy Solutions GmbH*), have a squared active area of 79.21 cm^2 (8.9 × 8.9 cm^2), with a Ni based anode, a NiO based cathode, a Li_2/K_2CO_3 electrolyte and an alumina based inert matrix; the exact composition of the materials cannot be disclosed due to confidentiality issues. Each cell was assembled sandwiching the electrolyte and the matrix sheets between anode and cathode first; then they were put between two current collectors, one for each side, and enclosed between two stainless steel frames to supply and expel the gas and to drain the collected current. The assembled cell was located inside the working station.

In order to properly validate the MCFC kinetics, different experimental tests were conducted. As in previous works [24,25], the number and the specificity of the tests were minimized on the basis of both background knowledge and aim of the work. The tests can be grouped as follows:

- Reference condition polarization curves,
- Study of the CO_2 effects at the cathode,
- Study of the O_2 effects at the cathode,
- Study of the H_2O effects at the cathode.

The different tested conditions are summarized in Table 2, while the reference one is shown in Table 3. The operating temperature was kept constant at the value of 923.15 K.

Starting from the reference cathode mixture (Table 3), the variation on the composition, in terms of content of each reactant