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An effective semi-empiric model for MCFC kinetics: Theoretical development and experimental parameters identification

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ABSTRACT

The aim of this work is to develop a semi-empirical model of the kinetics of MCFCs for laboratory and industrial simulation.

The rigorous theoretical approach takes into account the polarisation due to chemical as well as physical phenomena, but the number of parameters to be identified in the kinetic formulation has been reduced to the minimum in order to obtain an effective and accurate but, nevertheless, simplified instrument.

Validation has been performed thanks to experimental tests carried out at the Fuel Cell Centre laboratories of the Korea Institute of Science and Technology (KIST) using 100 cm² single cell facilities. *I*–*V* curves, EIS and gas analyses have furthermore been carried out to support the investigation.

A method for the parameter identification has been proposed on the basis of temperature, partial pressures and current density effects on performance.

Both experimental and theoretical results will be discussed in detail, presenting the resulting simulation tool as an effective instrument for the design, optimisation of operating conditions, diagnosis and control of MCFC devices.

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Introduction

Molten Carbonate Fuel Cells have reached the stage of commercialisation and are now ready for the challenge of market penetration. Nevertheless, new innovative applications, such as the use of non-conventional fuels or their integration in a Carbon Capture and Storage system, have given new importance to research activities.

Experience has shown that research activity can be effectively supported by a parallel process of experimentation and simulation, in a continuous and mutual system of verification and support.

Predictive simulation can help plan new technological solutions and optimise operating conditions, while on-time simulation is a good control tool for plant running.

In addition, the simulation of specific design performance is necessary for explaining and classifying experimental

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results and can be a very cost-effective method of saving on expensive experiments.

The benefits of the simulation approach are also applicable to MCFC research for the development of competitive products [1].

In our previous studies a kinetic formulation, which attempted to guarantee a theoretical consistency as well as an empirical approach based on experimental validation, had been proposed [2,3].

Here an analysis of MCFC polarization contributions is proposed following the authors' previous approach, but on the basis of more in-depth theoretical investigation and more extensive experimental campaign with the aim of obtaining an effective and accurate but nonetheless simplified tool which could be useful as the core of an industrial performance simulation process.

For the theoretical development, well known equations have been adopted, but with the intention of producing a formulation analogous with chemical reactions, in order to follow the traditional approach of chemical engineering, now that MCFCs are leaving laboratories to enter into the process engineering world.

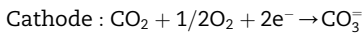
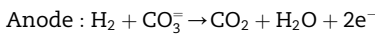
The experimental campaign was set up to attempt to isolate the different phenomena involved in MCFC kinetics and reduce the complexity of the electrodes.

The formulation obtained has been integrated as a new kinetic core in the SIMFC (SIMulation of Fuel Cells) code set up by the UNIGE PERT, which allows the simulation of MCFC behaviour on the basis of local mass, energy, charge and momentum balances [4].

Theoretical development

Thermodynamic approach

The thermodynamic equilibrium of a chemical reaction is identified by the well-known condition $\sum \nu_i \mu_i = 0$. A similar approach is used here to study the equilibrium condition of an electrochemical reaction. Referring to the specific case of MCFCs and starting from the half-reactions at the electrodes:



it can be seen that the equilibrium can be identified by the condition: $\sum \nu_j \mu_j^* = 0$ (where the counter "j" stands for both the chemical and electrochemical components). In particular, at the anode the CO_3^- ions are received producing a difference of potential between metal (-) and solution, therefore:

$$\nu_{\text{H}_2} \mu_{\text{H}_2}^* + \nu_{\text{CO}_3^-} \mu_{\text{CO}_3^-}^* + \nu_{\text{H}_2\text{O}} \mu_{\text{H}_2\text{O}}^* + \nu_{\text{CO}_2\text{AN}} \mu_{\text{CO}_2\text{AN}}^* + \nu_{\text{eAN}} \mu_{\text{e}}^* = 0 \quad (1)$$

Expliciting the chemical potential (μ) and the electrochemical potential, the result is:

$$\nu_{\text{H}_2} \mu_{\text{H}_2} + \nu_{\text{CO}_3^-} \text{FE}_S \text{ZCO}_3^- + \nu_{\text{H}_2\text{O}} \mu_{\text{H}_2\text{O}} + \nu_{\text{CO}_2\text{AN}} \mu_{\text{CO}_2\text{AN}} + \nu_{\text{eAN}} \text{FE}_{\text{AN}} \text{Z}_e = 0 \quad (2)$$

Similarly, at the cathode the production of CO_3^- ions generates a potential difference between the metal (+) and the solution, which at equilibrium follows the equation:

$$\nu_{\text{CO}_2\text{CAT}} \mu_{\text{CO}_2\text{CAT}} + \nu_{\text{O}_2} \mu_{\text{O}_2} + \nu_{\text{eCAT}} \text{FE}_{\text{CAT}} \text{Z}_e + \nu_{\text{CO}_3^-} \text{FE}_S \text{ZCO}_3^- = 0 \quad (3)$$

Summing the two expressions we obtain:

$$\sum_i \nu_i \mu_i + \nu_{\text{CO}_3^-} \text{FE}_S \text{ZCO}_3^- + \nu_{\text{eAN}} \text{FE}_{\text{AN}} \text{Z}_e + \nu_{\text{eCAT}} \text{FE}_{\text{CAT}} \text{Z}_e + \nu_{\text{CO}_3^-} \text{FE}_S \text{ZCO}_3^- = 0 \quad (4)$$

where "i" stands only for the chemical components.

Observing that:

$$\nu_{\text{CO}_3^-} = -\nu_{\text{CO}_3^-} \quad (5)$$

$$\nu_{\text{eAN}} = -\nu_{\text{eCAT}} \quad (6)$$

then:

$$\sum_i \nu_i \mu_i = \nu_{\text{eCAT}} \text{Z}_e F (E_{\text{CAT}} - E_{\text{AN}}) = \nu_{\text{eCAT}} \text{Z}_e F \Delta E \quad (7)$$

which refers to the thermodynamic statements:

$$dG|_{T,P} = -\delta L_{\text{max}}^* \quad (8)$$

which is the maximum electrical work.

Therefore, according to Denbigh for perfect gases (at low pressure) it is:

$$\sum_i \nu_i \mu_i^0 + RT \ln \prod_i p_i^{\nu_i} = \nu_{\text{eCAT}} \text{Z}_e F \Delta E \quad (9)$$

where:

$$\sum_i \nu_i \mu_i^0 = \nu_{\text{eCAT}} \text{Z}_e F \Delta E^0 \quad (10)$$

therefore:

$$\Delta E = \Delta E^0 + \left(\frac{RT}{\nu_{\text{eCAT}} \text{Z}_e F} \right) \ln \prod_i p_i^{\nu_i} \quad (11)$$

which, substituting the numerical values that refer to the electrical charges, is:

$$\Delta E = \Delta E^0 - \left(\frac{RT}{2F} \right) \ln \prod_i p_i^{\nu_i} \quad (12)$$

which is the equilibrium condition known as Nernst equation.

Kinetic approach

Just as we proceeded from a thermodynamic point of view, we can also deal with the kinetics. Therefore, for each half-reaction:

$$\nu_r = \nu_r' - \nu_r'' = k_{\text{kin}}' \prod_i C_{\text{isur}}^{\alpha_i'} - k_{\text{kin}}'' \prod_i C_{\text{isur}}^{\alpha_i''} \quad (13)$$

where C_{isur} are the concentrations of the chemical species "i" at the electrode surface and k_{kin}^* is the electrochemical kinetic constant.

Using the empirical Arrhenius equation gives us the dependence of the chemical kinetic constant on the temperature, generally written as:

$$k_{\text{kin}} = A e^{(-E_{\text{act}}/RT)} \quad (14)$$

it is possible to use this equation considering k_{kin}^* referred to E_{act}^* , as activation energy due to both the chemical and the electrochemical contributions. Therefore:

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