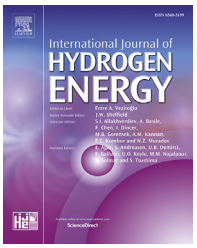
INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2018) 1–14

Available online at www.sciencedirect.com

ScienceDirect

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



A model for direct ethanol fuel cells considering variations in the concentration of the species

M.M. De Souza, R.S. Gomes, A.L. De Bortoli[*]

Federal University of Rio Grande do Sul, Av. Bento Gonçalves 9500, PO Box 15080, Porto Alegre, RS, 91509-900, Brazil

ARTICLE INFO

Article history:
Received 15 March 2018
Received in revised form
27 April 2018
Accepted 16 May 2018
Available online xxx

Keywords:
Direct ethanol fuel cell
Finite element method
Overpotential losses
Mole fraction of species
Ethanol

ABSTRACT

The fuel cell is an electrochemical device that converts chemical energy directly into electricity and is more efficient than traditional power generators. In this work, we developed a mathematical model for a direct ethanol fuel cell (DEFC), which considers the flow and concentration of species dependent on time and space for the calculation of losses overpotentials. In addition, the concentration of each species is modeled according to the current density of the DEFC. The finite element method is used to calculate the flow and concentration of the species in different layers of the cell (inlet and outlet channels, diffusion layer and catalyst layer). The model takes into account the losses overpotentials at the anode and at the cathode and the passage of ethanol through the membrane. The voltage and power density of the cell are calculated with different catalysts, temperatures and concentrations of ethanol. A result is shown for limiting current density for low ethanol concentrations. The results obtained compare favourably with the data found in the literature.

Introduction

Fuel cell is an electrochemical device that converts the chemical energy present in fuels directly into electrical energy. Among the main advantages of a fuel cell, there is the convenience of the instant recharge (the cell produces electricity as long as there is fuel), low emission of pollutants into the atmosphere, and is silent, compact and light. Fuel cells provide clean energy and high efficiency in a wide variety of applications [1]. The efficiency of fuel cells is generally greater than 50%, i.e. higher compared to internal combustion engines, which have about 30% efficiency with gasoline and about 50% with diesel.

Most studies done on fuel cells have focused on cells that use hydrogen as their source of energy. However, hydrogen can be obtained through fossil fuels or by electrolysis of water [2]. Another problem in the use of hydrogen is the availability of efficient storage and infrastructure technologies for its transportation and distribution. The use of liquid fuels in fuel cells, such as ethanol and methanol, would reduce the need to establish new infrastructure as required for hydrogen, but methanol is toxic, and its use on a large scale can cause serious environmental problems [3,4]. Therefore, ethanol obtained from biomass appears as a viable alternative because it is a renewable fuel with good potential for application in fuel cells.

Oil, coal and natural gas are currently the most used fuels in the world, accounting for about 80% of the world's energy mix. As they are not renewable, the burning of these fuels contributes directly to global warming and acid rain, among other problems. Non-renewable energy sources are at risk of

* *Corresponding author.*
E-mail address: dbortoli@mat.ufrgs.br (A.L. De Bortoli).

https://doi.org/10.1016/j.ijhydene.2018.05.096
0360-3199/

scarcity, as energy consumption has been increasing over time: currently around 2% per year.

The use of biomass became popular with increasing concern to improve techniques for the production and exploration of renewable energy sources, due to future shortages of traditional resources such as oil and coal. The rapid increase in global consumption of fossil fuels in the twentieth century suggests that depletion begins to undermine oil and natural gas reserves. This will result in increased use of alternative energy derived from biomass [5].

Ethanol is a renewable fuel that can be produced from biomass. Different forms of ethanol production from biomass were analysed. However, in general, the biomass is converted to ethanol through two chemical reactions: hydrolysis and fermentation. In some countries, such as Brazil and the USA, there is already a pre-established infrastructure for ethanol, which can easily be adapted to the fuel cell vehicle industry.

Interest in direct ethanol fuel cells (DEFCs) has grown considerably due to the higher energy density of ethanol, to be produced from renewable sources, to have lower rate of fuel passing through the membrane and to affect cathode performance less severely than methanol [6,7]. A DEFC works well and is considered a promising energy transformation equipment [8].

Fuel cells have attracted the interest of researches and industries in recent years. The most common practice in developing a new device is the use of experiments. But in addition to experiments, the mathematical modeling of fuel cells has helped in the design and optimization of these. In addition, the use of mathematical models makes the process faster and cheaper. Some studies using the finite element method for numerical simulations in Proton Exchange Membrane (PEM) fuel cells are found in the literature [9–11]. Most of these studies make use of one-dimensional models to approximate the flow in the different layers of DEFCs. According to Abdullah et al. [12], the DEFC development still requires a multidimensional and multiphase model capable of describing complex physical and chemical phenomena within the DEFC.

Several models for DEFCs are found in the literature. Some of them describe the physical behavior of the DEFC, but without considering spatial distribution of the variables [13,14]. Most of these models are one-dimensional. Andreadis et al. [15] presented a model that relates mass transport and electrochemical phenomena. Pramanik and Basu [16] developed a model that considers the effects of overpotential losses on DEFCs. Another one-dimensional model is that of Suresh and Jayanti [17], which study the effects of fuel passing through the membrane. Few papers deal with two or three dimensions. Heysiattalab and Shakeri [7] developed an analytical model for a two-dimensional (2D) DEFC. Yang et al. [18] presented a two-dimensional model that couples the mass transport and the electrochemical reactions in an alkaline direct ethanol fuel cell. Sarris et al. [19] and Gomes and De Bortoli [20] presented a three-dimensional model that studies the flow in the anode of a DEFC.

This paper presents a two-dimensional model for calculating the velocity field and concentrations of species in time and space (fuel consumption and products formation) on the anode and cathode sides of a DEFC. The velocity of the flow obtained by the model is inserted in the calculation of the overpotential losses and the concentrations. The model considers the calculation of the passage of ethanol through the membrane and the overpotential losses, and their influence on the operating voltage of the cell. In the calculation of these losses, which occur mainly due to activation, ohmic resistance and concentration, the species concentration on the surface of the catalyst is considered according to the current density.

The numerical results are obtained using the finite element method, which is known to have good theoretical basis mathematics [21,22]. The equations are considered transient, and are discretized by the Crank-Nicolson method.

The results show the flow velocity profile in the DEFC, the concentration of the main species, the dependence of the molar fraction of the species according to the current density, and the residual heat in relation to the current density. In addition, with the concentration of ethanol obtained through the 2D model, the limiting current density for the concentration of ethanol used in the DEFC is obtained. The results of voltage and power of the DEFC for different temperatures, catalysts and ethanol concentrations are compared with experimental data and present good agreement.

Direct ethanol fuel cell

Direct ethanol fuel cells (DEFCs) belong to the family of proton exchange membrane fuel cells (PEMFCs), in which ethanol is used directly as fuel [23].

In a typical direct ethanol fuel cell, the ethanol-water mixture is inserted into the anode side, which reacts to form carbon dioxide, protons, and electrons. The protons pass to the cathode through the membrane and the electrons through an external circuit, providing a potential difference. On the cathode side, the air reacts with the protons and electrons formed at the anode to produce water vapor [24]. The electrochemical reactions that occur inside the cell are given by Ref. [6]:

$$C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e^- \quad \text{at the anode,} \tag{1}$$

$$3O_2 + 12H^+ + 12e^- \rightarrow 6H_2O \quad \text{at the cathode,} \tag{2}$$

corresponding to the overall reaction

$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O. \tag{3}$$

The complete oxidation of ethanol is complicated by difficulty in breaking C–C bonds, to form intermediates that are absorbed into the catalyst surface. Generally, the electro-oxidation of ethanol in fuel cells is made using Pt based bimetallic catalysts. Goel and Basu [9] proposed a three-step mechanism for the electro-oxidation of ethanol using PtRu/C catalyst, as follow:

$$C_2H_5OH + Pt \rightarrow (C_2H_5OH)_{ad,Pt} \rightarrow (CH_3CHO)_{ad,Pt} + 2H^+ + 2e^- \tag{4}$$

$$3H_2O + 3Ru \leftrightarrow 3(OH)_{ad,Ru} + 3H^+ + 3e^- \tag{5}$$

$$(CH_3CHO)_{ad,Pt} + 3(OH)_{ad,Ru} \rightarrow 2CO_2 + 7H^+ + 7e^- + Pt + 3Ru. \tag{6}$$

In the first step, the ethanol is adsorbed on the surface of the cell catalyst, releasing electrons and protons. In step two, the dissociation of water occurs in the ruthenium catalyst. In step three, the interaction between the two adsorbed species forms carbon dioxide.

Please cite this article in press as: De Souza MM, et al., A model for direct ethanol fuel cells considering variations in the concentration of the species, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2018.05.096