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A three-dimensional non-isothermal model for a membraneless direct methanol redox fuel cell

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HIGHLIGHTS

- A numerical model for a membraneless direct methanol redox fuel cell is developed.
- Model results provide detailed insight into the electrochemical-thermal process.
- The 3D electrodes reduce the reactant crossover but impede the removal of products.
- The porosity of anode media shows more significant effects than that of cathode.
- The product CO_2 shows effects on the reactant transport and the cell performance.

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ABSTRACT

In the membraneless direct methanol redox fuel cell (DMRFC), three-dimensional electrodes contribute to the reduction of methanol crossover and the open separator design lowers the system cost and extends its service life. In order to better understand the mechanisms of this configuration and further optimize its performance, the development of a three-dimensional numerical model is reported in this work. The governing equations of the multi-physics field are solved based on computational fluid dynamics methodology, and the influence of the CO_2 gas is taken into consideration through the effective diffusivities. The numerical results are in good agreement with experimental data, and the deviation observed for cases of large current density may be related to the single-phase assumption made. The three-dimensional electrode is found to be effective in controlling methanol crossover in its multi-layer structure, while it also increases the flow resistance for the discharging products. It is found that the current density distribution is affected by both the electronic conductivity and the concentration of reactants, and the temperature rise can be primarily attributed to the current density distribution. The sensitivity and reliability of the model are analyzed through the investigation of the effects of cell parameters, including porosity values of gas diffusion layers and catalyst layers, methanol concentration and CO_2 volume fraction, on the polarization characteristics.

1. Introduction

Methanol (MeOH), as a fuel, has high energy density and can be generated from many sources, among others, natural gas, coal, and biomass; when used in fuel cells, it allows continuous operation [1]. Direct methanol fuel cells (DMFCs) show great potential for their application in consumer electronic products. Over the past 1 to 2 decades, considerable research effort has been expended on DMFC-related technologies. However, to date there are still several challenges related to DMFCs, which require appropriate answers. Areas, among others, which require immediate attention are development of efficient and economical catalysts, restraint on fuel-crossover, extension of service life and cost reduction.

Lam et al. [2] reported a membraneless DMFC architecture and explored its performance improvement mechanisms relative to the traditional DMFC. In the membraneless DMFC, an open silicon separator with acid solution instead of a proton exchange membrane is used for the proton transport and a three-dimensional (3D) anode with multi-layered catalysts is applied to reduce methanol crossover. In the interior of the 3D anode structure, oxidation of methanol creates a localized concentration gradient leading to a lower concentration of methanol at the anode/cathode interface, so that the fuel crossover is

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Nomenclature

a	effective specific area in catalyst layer, m^{-1}
C	molar concentration, mol m^{-3}
c_p	specific heat at constant pressure, J kg^{-1} K^{-1}
D	diffusion coefficient, m^2 s^{-1}
E^0	standard potential, V
F	Faraday constant, 96485 C mol^{-1}
f_{CO2}	volume fraction of CO_2
i_o	exchange current density, A m^{-2}
j	volumetric reaction current density, A m^{-3}
K	permeability
k	thermal conductivity, W m^{-1} K^{-1}
M	molecular weight, kg mol^{-1}
n	number of electrons in electrochemical reaction; Bruggeman exponent
p	pressure, Pa
R	universal gas constant, 8.314 J mol^{-1} K^{-1}
S	source term in transport equation
s	stoichiometry coefficient in electrochemical reaction
T	temperature, K
U_o	equilibrium cell potential, V
u	fluid velocity, m s^{-1}

Greek characters

α	transfer coefficient
γ	reaction order
ε	porosity
η	overpotential, V
κ	ionic conductivity, S m^{-1}
μ	viscosity, Pa s
ρ	density, kg m^{-3}
σ	electronic conductivity, S m^{-1}
τ	shear stress, N m^{-2}
Φ	potential, V

Subscripts

a	anode
c	cathode
e	electrolyte
k	species index
N	Nafion
ref	reference value
s	solid

reduced even without a membrane configuration. In a later publication by Lam et al. [3], it was proposed an anaerobic membraneless DMFC, which combines membraneless 3D electrode structure with redox couple cathode to address the fuel-crossover issue. This membraneless DMFC is termed as membraneless direct methanol redox fuel cell (DMRFC). The redox couple cathode, utilized previously for proton exchange membrane fuel cell (PEMFC) [4–6], is deemed to be a promising approach to avoid using noble metal catalysts, and to improve cathode kinetics and reduce the impact of cathode flooding. The membraneless DMRFC was found to have a maximum power density that is ~35% higher than the Nafion® 117 based DMFC; moreover, the structure of the latter tends to be more complex with a relatively higher cost.

There are still challenges we have to resolve or confront for the membraneless DMRFC. Over extended operation, the output voltage of membraneless DMRFC may vary widely, most likely due to the blockage by the gas (CO_2) of the reactant/product pathways; therefore, the distribution of CO_2 in the interior of the fuel cell and its effects on reactants transport need to be analyzed. Based on the mass diffusion theory, the reactant concentration should decrease along the transverse direction, whereas the catalyst is evenly distributed in the multi-layered 3D electrode, which is inconsistent with the reactant distribution; therefore, it is necessary to improve the 3D electrodes structure to minimize the fuel crossover and to maximize the utilization of catalyst.

Numerical simulation is an effective and powerful method to understand the underlying physicochemical mechanisms of the involved multi-physics processes occurring in membraneless DMRFC, and, with the consequent knowledge, to design and optimize the 3D electrode structure. A fuel cell model encompasses five conservation laws dealing with mass, momentum, species, electrical charge and energy. The governing transport equations are written in the form of advection-convection diffusion source equations [7]. Wang and Wang [8] developed a multi-phase mixture (M^2) model for liquid-feed DMFC to predict methanol crossover caused by diffusion, convection and electro-osmosis. The model was then extended to 3D with an interfacial liquid coverage module used to account for the effect on the channel liquid flow [9,10]. It was found that the liquid coverage at the interface between backing layer and flow channel had a profound effect on the net water transport coefficient through the membrane. Since then, considerable progress was made on DMFC modeling; various models have led to better understanding of the involved multi-physical transport mechanisms and/or the development of new and advanced DMFCs, including the passive air-breath high concentration DMFC [11,12], the DMFC with micro-porous layer (MPL) [13,14] and the membraneless DMFC [15–18]. The membraneless design that relies on the fluid electrolyte, and the laminar flow regime was found to be able of restraining the methanol crossover and consequently leading to the increase of fuel utilization. However, to the best of our knowledge, no numerical model has ever been developed for the membraneless DMRFC.

The present work aims to develop a 3D model for non-isothermal transport and reaction processes occurring in the membraneless DMRFC with particular focus on the effect of open separator and 3D electrode structures on species concentration distribution and corresponding polarization characteristics. The present paper is organized as follows. Section 2 presents a brief mathematical description of the membraneless DMRFC model with particular focus on the transport in the open separator and effects of the CO_2 gas. In section 3, comparison between the simulation results and experimental data is conducted with the primary aim of validating the present model. A detailed performance analysis at three typical current density values is used to determine the eventual relationships among the key parameters related to the membraneless DMRFC. In addition, the effect of the CO_2 gas, porosity and concentration on the polarization characteristics is studied to analyze the sensitivity and reliability of the model.

2. Mathematical model

2.1. Membraneless DMRFC

The membraneless DMRFC tested by Lam et al. [3] is a single pass fuel cell with an active section area of 4 cm^2. 3D electrodes at anode and cathode both are implanted to extend the reaction zone and mitigate/eliminate the effect of crossover of reactants. At the anode, the 3D structure was made by stacking a BASF TGPH-60 carbon fiber paper (CFP) with 20% wet proofing and two layers with catalyst loading of 5 mg cm^{-2} Pt-Ru and 3 mg cm^{-2} Pt-Ru, respectively. The oxygen cathode is replaced by ion redox couple cathode, for which the reaction rate is significantly higher than that of the oxygen cathode, even without the use of a noble metal catalyst. The 3D cathode was