Comparison of Modeling Approaches in Direct Ethanol Fuel Cells

[1]A. Suhaila and [2]S.K. Kamarudin

[1]*Faculty of Chemical Engineering Technology, TATI University College Jalan Panchor Telok Kalong, 24000 Kemaman, Terengganu*
[2]*Fuel Cell Institute, University Kebangsaan Malaysia, 43600 Bangi, Selangor*

A R T I C L E   I N F O

A B S T R A C T

Direct Ethanol Fuel Cell (DEFC) are promising candidates as alternative energy conversion devices for transportation, stationary power and portable applications due to efficient, safe and reliable power solution. Mathematical models are a fundamental tool for the design process of DEFC and DEFC systems. Modeling and simulation are very useful tools in the study of complex DEFC system. They enable us to ascertain the impact of great variety of conditions and variables on the DEFC system's global or local operating point. The advantages of this modeling, is the user of the model can tests various hypotheses without the risk of deterioration or destruction of real system. This paper reviewed of recent DEFC modeling available in open literature. This reviewed can be divided to two manifolds. The first part discussed about previous mathematical modeling on DEFC including general modeling criteria. A few considerations need to taken into accounts in developed mathematical modeling such as model approaches, state of model, system boundary, spatial dimension, complexity and validation. The second part focused on modeling approaches that can be classified as analytical, semi-empirical and mechanistic. Semi-empirical and semi-analytical models are selected as case study in this part. Polarization curve and performance curve for both model are compared to the available experimental results in the literature. The semi-analytical model shows fairly a good agreement with experimental result compared to semi empirical model. However, semi analytical model only show a good agreement with experimental result at first region of polarization curve (activation loss region) not at second and third region (Ohmic losses and concentration losses region).This is due to ohmic losses only considered in membrane while in cathode side only single phase is considered which make inaccurate prediction model in concentration loss region. For semi-empirical model, the model show signs of deviating from experimental result at all regions. The reason for this is that the given model only considered concentration losses at anode side. For a one-dimensional case study, both methods were compared quantitatively and results show that semi-analytical models able to predict the performance of DEFC.

INTRODUCTION

The use of ethanol in fuel cell (FC) provides a highly effiecient conversion of the chemical energy in hydrocarbons and small scale energy production for stationary use. It is as promising candidate due to i) high power energy density (8.00kWhkg-1) is comparable to hydrocarbons and gasoline, ii)non toxicity iii) natural availability derived from biomass. In miniature applications, ethanol is reformed to hydrogen in the FC itself which known as Direct Ethanol Fuel Cell (DEFC). On the other hand, reformer reaction is required to separates hydrogen from an ethanol which will enlarge the size and weight of DEFC system. DEFC performance can be evaluated using experimental method or mathematical modeling. A numbers of experimental works had been carried out by researchers to investigate the DEFC performance focused on electrocatalyst and polymer electrolyte membrane properties(Andreadis, Stergiopoulos, Song, & Tsiakaras, 2010; Beyhan, Coutanceau, Léger, Napporn, & Kadırgan, 2013; Heysiattalab, Shakeri, Safari, & Keikha, 2011; Li, Y. S., Zhao, & Liang, 2009; Linares, Rocha, Zignani, Paganin, & Gonzalez, 2013). Nevertheless, the DEFC performance developments not only rely on the material development such as better catalyst or polymer electrolyte membrane , but also the optimal design related to the operating conditions, physical and electrochemical parameters and geometric design parameters including the passive ancillary systems. These parameters are coupled in the complex physiochemical process, including the heat/mass transport and multiple electrochemical equations (Xiao, Bahrami, & Faghri, 2010). Since it is hard to quantify the complex process inside a DEFC

Corresponding Author: A. Suhaila, Faculty of Chemical Engineering Technology, TATI University College Jalan Panchor Telok Kalong, 24000 Kemaman, Terengganu.

directly by experiments, the mathematical modeling can act as an effective design tool to investigate the physiochemical phenomena and performance characteristic of the DEFC. Besides, experimentation does not facilitate innovative design, limited to existing apparatus, costly and time consuming. Thus, mathematical modeling is favorable because it allows better comprehension of the fuel cell's design, operating parameters effect on performance, durability and operation (Andreadis, G. M., Podias, & Tsiakaras, 2008).There are a few considerations need to be taken into account to develop mathematical model as listed in table 1. The first row in the table listed three types of model approaches in FC depends on the system boundary. The system boundary as presented in table 1 defines the area of interest of the model. The particular area of interest could be the fundamental cell level including the electrodes and the membrane, the higher level with single cells assembled in a FC stack, or the high fuel cell system level composing of a FC stack with its auxiliary systems. The selection of state of the model either steady state or transient is related to the system boundary. Usually steady state model are useful for sizing components in the FC system, for calculating amounts of materials such as catalyst and parametric studies. While unsteady state model can be used for start-up and shutdown procedures, analysis of influences of various components on flow during a drive cycle and optimization of the response time on load changes. Spatial dimension and complexity/details are another important criteria. Mass and energy balances need to be developed to describe the process occurred in DEFC. Mass transport limitations phenomena in DEFC required spatial dimension features. The validations are crucial to ensure the proposed mathematical model is to be useful and reliable tool. Appropriate data either from experiments or previous published data are needed for validation. Our literature review indicates a significant amount of mathematical modeling has been published for direct methanol fuel cell (DMFC) ranging from 1D to 3D (Ismail, Kamarudin, Daud, Masdar, & Yosfiah, 2011; Oliveira, Falcao, Rangel, & Pinto, 2008; Xiao *et al.*, 2010; Yang, Zhao, & Xu, 2007; Zhao, Xu, Chen, & Yang, 2009), but only a few available for direct ethanol fuel cell in open literature. Thereby, this paper reviews some of the work done in DEFC, discusses and compared modeling approaches used in DEFC modeling.

Table 1: Key features of fuel cell model (Haraldsson & Wipke, 2004).

Model approach (Mechanistics, semi empirical and analytical)
State (steady state, unsteady state (transient)
System boundary (single cell, stack, system (balance of plant))
Spatial Dimension (0D, 1D, 2D, 3D)
Complexity/details (electrochemical, thermodynamic, fluid dynamics relationships)
Validations

Categories of Fuel Cell Model:

The DEFC model can be classified into three categories analytical, semi empirical or mechanistic model. The overview of available DEFC mathematical modeling in open literature according to their areas of investigation and system boundary is presented in table 2. In order to develop analytical model, many simplifying assumptions were made concerning variable profiles within the cell. Analytical models are approximate model to be used in simple design for quick calculations. Thus, the model not able to provide clear picture of transport processes occurring within the cell. Examples of analytical modeling of DEFCs are those reported by (Heysiattalab, 2011). Theoretical or mechanisctic model is developed from fundamental principles of physical-chemical relationships includes the conservation of mass and conservation of energy as well as reaction kinetics, transport phenomena and thermodynamics. Mechanistic models can be subcategorized into multi domain models or single domain (or unified) models. Single domain approach combines all the regions of interest into one domain. Conservation equations are defined which govern the entire fuel cell are written in the form of generic convection-diffusion equations. For all terms, which do not fit that format are dumped into the source or sink term. Example of mechanistic unified model is reported by (Sousa *et al.*, 2008) Multi-domain models are the derivation of different sets of equations for each region of the fuel cell. These equations are solved separately and simultaneously.An empirical model applied if the fundamental model is too complex or if the empirical model has satisfactory predictive capability. An example of an empirical model is a simple least squares fit of an equation to experimental data. Semi empirical model is compromise between mechanisctics and empirical model. Its combines theoretically derived differential and algebraic equations with empirically determined relationships. However, semi-empirical models are applicable for interpolation operating conditions only and cannot be extrapolated to outside of that range. Thus, it is cannot be used to predict the performance of innovative designs, or the response of the fuel cell to parameter changes outside of the conditions under which the empirical relationships were developed. Their applications are limited for making quick predictions for designs that existed. Examples of semiempirical model is reported by (Antolini & Gonzalez, 2010). The authors proposed simple model to evaluate the contribution of alloyed and non-alloyed platinum and tin to the ethanol oxidation reaction on Pt–Sn/C catalysts for direct ethanol fuel cells.The proposed model able to predict the performan material. Furthermore, the model shown the ethanol oxidation on partially alloyed catalysts occurs through a dual pathway mechanism, separately involving the Pt_3Sn phase and $Pt–SnOx$. Li, Y. S., Zhao, & Yang (2010) measured water uptake and transport properties such as water diffusivity, the electro-osmotic drag

(EOD) coefficient , mass transfer coefficient at cathode in anion exchange membrane (AEM-DEFC) using semi empirical modeling.
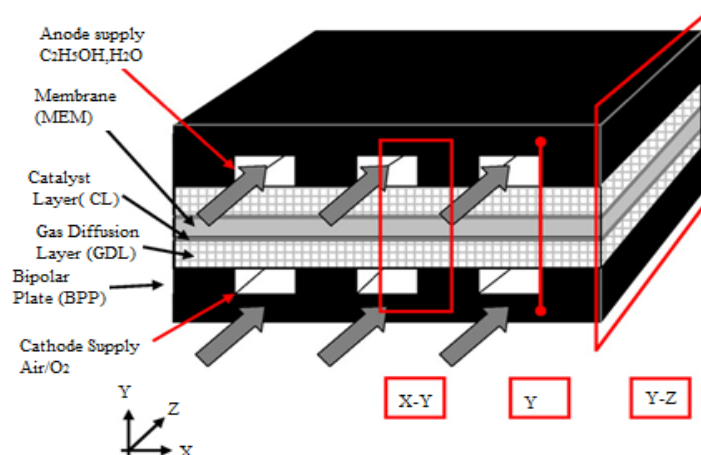
Spatial Dimension

Fig. 1: Schematic illustration of spatial dimension 1D(Y direction), 2D (X-Y/Y-Z direction), 3D (X-Y-Z direction) (Cheddie & Munroe, 2005).

Spatial dimension is important criteria to take into account in order to describe fuel cell phenomena such as mass transport limitation. FC Spatial dimension is ranging from one dimension to three dimension as illustrated in figure 1. At the earlier of fuel cell modeling, researchers used one dimensional (1D) models in the y direction (sandwich) with a range of degrees of complexity. FC operating parameters were analyzed for given boundary conditions and were taken to be normal to the computational subdomains. 2D models either in the x-y or y-z direction offers more realistic view of certain phenomena as spatial variations are taken into account. If the overall DEFC behavior is of interest, 3D models (x–y–z direction) sandwich domain are the best. 1D and 2D models may include the same conservation equations as three-dimensional (3D) model.

1D model:
Previously, many researchers developed mathematical model using 1D model as it able to provide much information with sufficient accuracy if the boundary and initial conditions are carefully selected(Siegel, 2008). The operating parameters such as cell temperature, ethanol feed concentration on PEM-DEFC's performance and ethanol crossover using 1D mathematical modeling are widely investigated (G.M. Andreadis *et al*., 2008; G.M. Andreadis, Podias, & Tsiakaras, 2009; George Andreadis & Tsiakaras, 2006; Suresh & Jayanti, 2011)(Pramanik & Basu, 2010).Verma & Basu, (2007) developed 1D mathematical modeling of direct alkaline fuel cell using various alcohol. The model taken into account activation, ohmic and concentration overpotentials losses in predicting FC performances. The comprehensive mathematical model by taking into account multistep EOR, transport process and mixed potential was developed to enable deep insights in crucial process such as ethanol crossover and the incomplete ethanol oxidation (Meyer, Melke, & Gerteisen, 2011). In order to reduced ethanol crossover effect, a multi layer membrane was proposed by Bahrami & Faghri, (2012). The authors developed physical model to investigate the effectiveness of employed membrane in AEM-DEFC.

2D:
There are very limited published paper devoted on 2D modeling in DEFC. Heysiattalab *et al* (2011) developed 2D analytical model for investigate DEFCs performances with assumptions fluid flows in steady state, isothermal. The developed model is precise in activation and ohmic loss region only. The neglecting of concentration loss and increasing ethanol inlet concentration make this model inaccurate in third region (concentration loss region). Thus, a model only capable to estimate polarization curve up to 0.5M at anode and cathode. Sousa *et al* (2008) developed mechanistic model on the basis realistic EOR mechanism that considers the formation of acetaldehyde and acetic acid as product. Thi multiple EOR mechanism on Pt catalyst at anode. The anode mathematical model was derived from material balances for each species in solution. The simulation result shown the concentration profiles of acetaldehyde and acetic acid is agreed with experimental result.

3D:
3D models is a combination of both 2D computational domains and have the ability to investigate the blocking effect of the bipolar plates, detailed current density distribution or the effectiveness flow field design. The only work was presented by Sarris, Tsiakaras, Song, & Vlachos (2006). The authors investigated the flow field and residence time in the anode flow bed of DEFCs using 3D numerical flow modeling in Computational

Fluid Dynamics (CFD) software. The studied main goal is to assess the ability of the CFD model in predicting physical and transport process in Fuel Cell (FC). The multiphase effect, non isothermal and isobaric are considered in this model. The flow field and residence time in anode were evaluated in three 3 different Reynolds Number (Re). For very low Re (Re =1), creeping flow is observed showing that not capable to enhance mixing. However, for higher Re, the flow is overoptimistics which make inappropriate for bed design because slow reaction rates demand slow fluid motion. This evident that the present anode bed design (2cm x 2cm x 2mm) does not satisfy the requirement of homogeneous flow distribution over the electrodes. In order to obtain optimum bed design, the mixture velocity should remain as low in flow bed compartment to produce circulations, thus increasing residence time, in a homogenous way to give a balanced use of the catalyst.
Case Study – semi-analytical and semi-empirical examples

In this section, two selected DEFC models are compared; the semi-analytical model of Suresh & Jayanti, (2011) and the semi-empirical approach of George Andreadis & Tsiakaras (2006). This to models are compared for PEM-DEFC at T=75^{0}C and 90^{0}C with PtSn/C at anode and Pt/C at Cathode. The experimental data with same MEA configurations in open literature is used to validate the model. However, for the polarization curve figure the operating temperature for experimental data is 70^{0}C which less than model.

Semi- analytical Model:
The assumptions used in this one-dimensional isothermal model are:
- The cell operates under steady state
- Variations in one spatial coordinate(z), perpendicular to MEA
- Negligible pressure gradient across the membrane and catalyst poisoning
- Complete oxidation reaction, no intermediate products formed at ACL
- Flow fields are assumed to be thoroughly mixed.
- The catalyst layers are assumed to be macro homogeneous porous electrode, hence the chemical reactions is considered as homogenous.
- Carbon dioxide is assumed to be fully dissolved, thus carbon dioxide permeation across electrolyte membrane is neglect.
- The electrolyte is assumed to be fully saturated
- The electrochemical reactions governed by Butler-Volmer kinetics.
- Multi component gaseous mixture is considered in the cathode side.
- Only water vapor is considered on the cathode side.
- The voltage losses due to electronic resistance is neglect.
- The anodic and cathodic overpotentials are considered constant throughout catalayst layer.

The authors developed the mass transfer equations separately for each regions namely; anode and cathode flow field, anode backing layer (ABL), anode catalyst layer (ACL) , polymer electrolyte membrane (PEM), cathode backing layer (CBL) and cathode catalyst layer (CCL). The Butler-Volmer equation describes the rate of electrochemical reaction in the anode while Tafel type at the cathode. The complete set of equations including the set of parameters used can be found in (Suresh & Jayanti, 2011)

Semi-empirical model:
The cell voltage is calculated by the theoretical open voltage less the anode overpotential less the potential loss in membrane and less contact resistance in DEFC for this semiempirical model. The assumptions used in this steady state, and one-dimensional model are:
- The cell operates in isothermal conditions.
- The pressure at both anode and cathode are equal to atmospheric pressure.
- The anode overpotential is calculated using semi empirical equation by fitting equations to data found in literature.
- The ethanol crossover is the combination of electroosmosis and diffusion phenomena, is obtained from a semi empirical expression.
- Potential loss in the membrane and contact resistance is determine from semiempirical equations with parameter value obtained from previous experiments.

RESULT AND DISCUSSION

In this section, polarization curve and performance curve for both model are presented. To compare the precision of these 2 models, the available experimental results in the literature are plotted. Figure 2 shows the comparison of polarization curve for semi empirical model and semi-analytical model against the experimental result. Obviously, semi-analytical model shows fairly a good agreement with experimental result compared to semi empirical model. However, semi analytical model only show a good agreement with experimental result at

first region of polarization curve (activation loss region). For second and third region (Ohmic losses and concentration losses region), the semi analytical model not precisely predicting the cell performance. This is due to ohmic losses only considered in membrane while in cathode side only single phase is considered which make inaccurate prediction model in concentration loss region. For semi-empirical model, the model show signs of deviating from experimental result at all regions. The reason for this is that the given model only considered concentration losses at anode side.

Table 2: Summary of previous DEFC mathematical modeling

Authors	System Boundary	Approaches	Spatial dimension	State	Parameters Studied				
	Single /Stack/System	Analytical/ Empirical/ Mechanistic	1D/2D/3D	ss/TR	Component Concentration	Catalyst Utilization	Membrane properties	CO kinetics	Water Properties
G.Anreadis *et al* (2006)	Anode PEM-DEFC	Empirical	1D	ss	Ethanol	Catalyst Thickness	Protonic Conductivity	No	No
G.Anreadis, P.Tsiakaras (2006)	PEM-DEFC	Empirical	1D	ss	Ethanol	Catalyst Thickness	volume fraction	No	No
S.Basu (2007)	AEM-DEFC	Analytical	1D	ss	Ethanol	No	Electrolyte concentration	No	No
R.Sousa Jr.*et al* (2008)	Anodic process PEM-DEFC	Mechanistic	2D	ss	Ethanol,Water Water,Acetic acid CO_2 Acetaldehyde	Catalyst surface	No	No	mass transfer coefficient water uptake EOD coefficient
G.M Andreadis (2008)	PEM-DEFC	Empirical	1D	ss	Ethanol,	No	No	No	No
G.M Andreadis (2009)	PEM-DEFC	Empirical	1D	ss	Ethanol	Pt loading, specific reaction surface area	thickness	No	No
E.Antolini (2010)	catalyst PEM-DEFC	Analytical	NA	NA	No	Catalyst model	No	No	No
Y.S.Li (2010)	Water properties correlation for AEM-DEFC	Analytical	NA	NA	No	No	No	No	No
S.Basu (2010)	PEM-DEFC	Analytical	1D	ss	Ethanol	No	No	No	No
S.Jayanti (2011)	PEM-DEFC	Analytical	1D	ss	Ethanol	No	No	No	No
Saeed Heysiattalab (2011)	PEM-DEFC	Analytical	2D	ss	Ethanol	No	No	No	No
H.Bahrami (2012)	AEM-DEFC	Analytical	1D	ss	Ethanol	No	Membrane thickness	No	No

Figure 3 shows the power density performance of both models and experimental at operating temperature is 90^0C. Semi empirical model shows the highest value of peak power density which is predominantly deviate from experimental result. On the other hand, semi-analytical model shows a good agreement with experimental data. This is because, the applications of Tafel kinetics expression at anode, simultaneous ethanol oxidation and oxygen reduction at cathode. Furthermore, the considerations mixed potential effects in semi analytical model able to predict DEFC performance as good as experimental data.
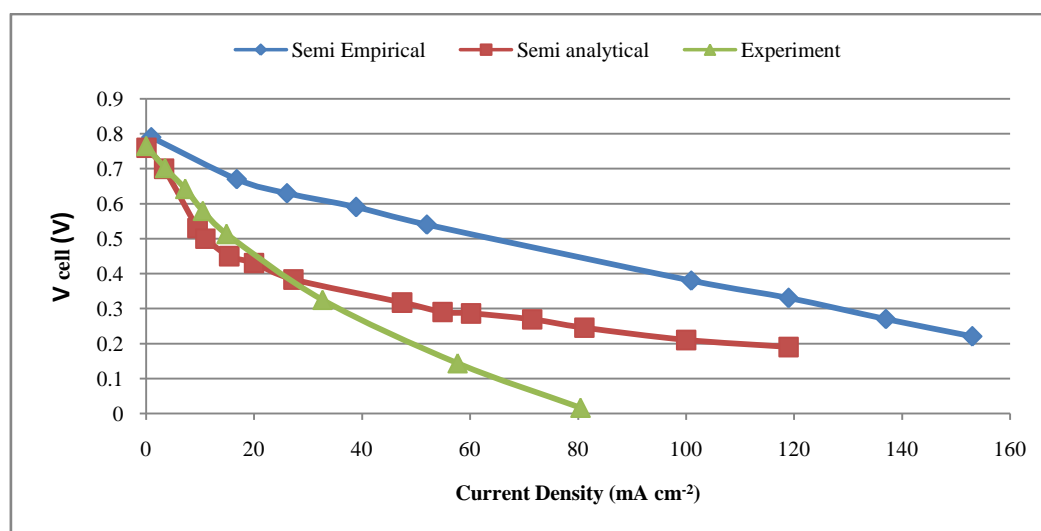

Fig. 2: Polarization curve.for semi empirical model, semi-analytical(anode PtSn/C, cathode Pt/C, ethanol feed = 1.0M, T = 75^0C) and experimental data(anode PtSn/C, cathode Pt/C, ethanol feed = 1.0M, T = 70^0C).
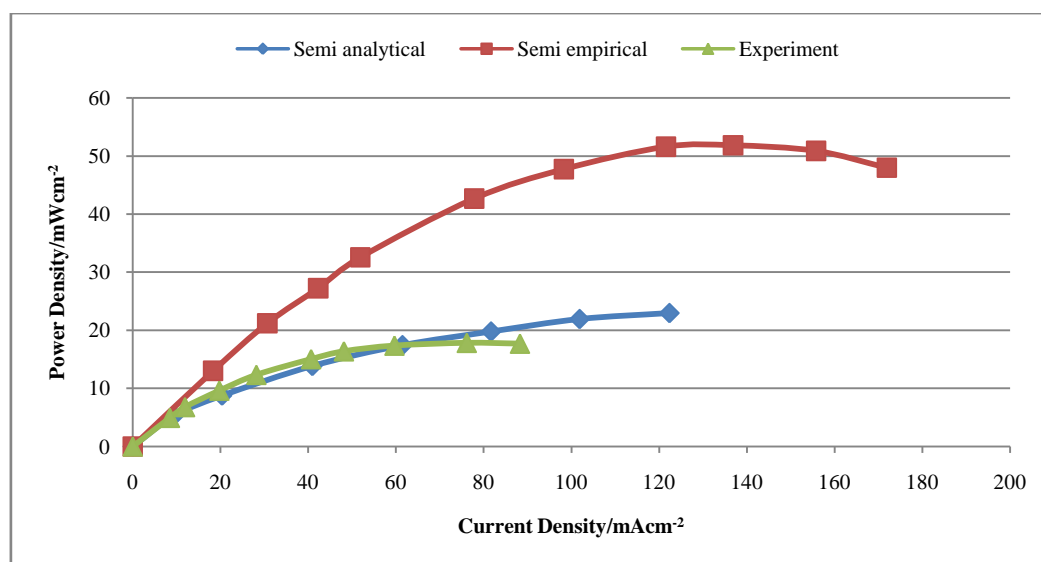
Fig. 3: Polarization curve.for semi empirical model, semi-analytical and experimental data (anode PtSn/C, cathode Pt/C, ethanol feed = 1.0M, T = 90^{0}C).

Conclusions:

A review of DEFC modeling was presented. Fuel cell models can be categorized as analytical, semi-empirical or mechanistic. The model of Suresh & Jayanti (2011) (semi-analytical) and George Andreadis & Tsiakaras (2006) (semi-empirical) was taken as case study. In order to validate the proposed mathematical model, the previous experimental result by (Zignani, Gonzalez, Baglio, Siracusano, & Aricò, 2012) and Lee, Murthy, & Manthiram, (2011) was compared. The semi analytical is fairly predicted the polarization behavior and cell performance. While for semi-empirical model, the proposed model is deviated from experimental result. It shows that semi analytical model that are based on experimental data at least at some extent, able to provide a fast start into DEFC modeling and a good basis for engineering applications.

REFERENCES

Andreadis, G., V. Stergiopoulos, S. Song, P. Tsiakaras, 2010. Applied Catalysis B : "Environmental Direct ethanol fuel cells : The effect of the cell discharge current on the products distribution". *"Applied Catalysis B, Environmental"*, 100(1-2): 157-164.

Andreadis, G.M., A.K.M. Podias, P.E. Tsiakaras, 2008. "The effect of the parasitic current on the Direct Ethanol PEM Fuel Cell Operation". *Journal of Power Sources*, 181(2): 214-227.

Andreadis, G.M., A.K.M. Podias, P.E. Tsiakaras, 2009. "A model-based parametric analysis of a direct ethanol polymer electrolyte membrane fuel cell performance". *Journal of Power Sources*, 194(1): 397-407.

Andreadis, George, P. Tsiakaras, 2006. "Ethanol crossover and direct ethanol PEM fuel cell performance modeling and experimental validation". *Chemical Engineering Science*, 61(22): 7497-7508.

Antolini, E., E.R. Gonzalez, 2010. "A simple model to assess the contribution of alloyed and non-alloyed platinum and tin to the ethanol oxidation reaction on Pt–Sn/C catalysts: Application to direct ethanol fuel cell performance". *Electrochimica Acta*, 55(22): 6485-6490.

Bahrami, H., A. Faghri, 2012. "Multi-layer membrane model for mass transport in a direct ethanol fuel cell using an alkaline anion exchange membrane". *Journal of Power Sources*, 218: 286-296.

Beyhan, S., C. Coutanceau, J.M. Léger, T.W. Napporn, F. Kadırgan, 2013. "Promising anode candidates for direct ethanol fuel cell: Carbon supported PtSn-based trimetallic catalysts prepared by Bönnemann method". *International Journal of Hydrogen Energy*, 38(16): 6830-6841.

Cheddie, D., N. Munroe, 2005. "Review and comparison of approaches to proton exchange membrane fuel cell modeling". *Journal of Power Sources*, 147(1-2): 72-84.

Haraldsson, K., K. Wipke, 2004. "Evaluating PEM fuel cell system models". *Journal of Power Sources*, 126(1-2): 88-97.

Heysiattalab, S., 2011. "2D Analytical Model for Direct Ethanol Fuel Cell Performance Prediction". *Smart Grid and Renewable Energy*, 02(04): 427-433.

Heysiattalab, S., M. Shakeri, M. Safari, M.M. Keikha, 2011. "Investigation of key parameters influence on performance of direct ethanol fuel cell (DEFC)". *Journal of Industrial and Engineering Chemistry*, 17(4): 727-729.

Ismail, A., S.K. Kamarudin, W.R.W. Daud, S. Masdar, M.R. Yosfiah, 2011. "Mass and heat transport in direct methanol fuel cells". *Journal of Power Sources*, 196(23): 9847-9855.

Lee, E., A. Murthy, A. Manthiram, 2011. "Effect of Mo addition on the electrocatalytic activity of Pt–Sn–Mo/C for direct ethanol fuel cells". *Electrochimica Acta*, 56(3): 1611-1618.

Li, Y.S., T.S. Zhao, Z.X. Liang, 2009. "Performance of alkaline electrolyte-membrane-based direct ethanol fuel cells", 187: 387-392.

Li, Y.S., T.S. Zhao, W.W. Yang, 2010. "Measurements of water uptake and transport properties in anion-exchange membranes". *International Journal of Hydrogen Energy*, 35(11): 5656-5665.

Linares, J.J., T.A. Rocha, S. Zignani, V.A. Paganin, E.R. Gonzalez, 2013. "Different anode catalyst for high temperature polybenzimidazole-based direct ethanol fuel cells". *International Journal of Hydrogen Energy*, 38(1): 620-630.

Meyer, M., J. Melke, D. Gerteisen, 2011. "Modelling and simulation of a direct ethanol fuel cell considering multistep electrochemical reactions, transport processes and mixed potentials". *Electrochimica Acta*, 56(11): 4299-4307.

Oliveira, V., D. Falcao, C. Rangel, A. Pinto, 2008. "Heat and mass transfer effects in a direct methanol fuel cell: A 1D model". *International Journal of Hydrogen Energy*, 33(14): 3818-3828.

Pramanik, H., S. Basu, 2010. "Modeling and experimental validation of overpotentials of a direct ethanol fuel cell". *Chemical Engineering and Processing: Process Intensification*, 49(7): 635-642.

Sarris, I., P. Tsiakaras, S. Song, N. Vlachos, 2006. "A three-dimensional CFD model of direct ethanol fuel cells: Anode flow bed analysis". *Solid State Ionics*, 177(19-25): 2133-2138.

Siegel, C., 2008. "Review of computational heat and mass transfer modeling in polymer-electrolyte-membrane (PEM) fuel cells". *Energy*, 33(9): 1331-1352.

Sousa, R., D.M. dos Anjos, G. Tremiliosi-Filho, E.R. Gonzalez, C. Coutanceau, E. Sibert, K.B. Kokoh, 2008. "Modeling and simulation of the anode in direct ethanol fuels cells". *Journal of Power Sources*, 180(1): 283-293.

Suresh, N.S., S. Jayanti, 2011. "Cross-over and performance modeling of liquid-feed Polymer Electrolyte Membrane Direct Ethanol Fuel Cells". *International Journal of Hydrogen Energy*, 36(22): 14648-14658.

Verma, A., S. Basu, 2007. "Experimental evaluation and mathematical modeling of a direct alkaline fuel cell". *Journal of Power Sources*, 168(1): 200-210.

Xiao, B., H. Bahrami, A. Faghri, 2010. "Analysis of heat and mass transport in a miniature passive and semi passive liquid-feed direct methanol fuel cell". *Journal of Power Sources*, 195(8): 2248-2259.

Yang, W.W., T.S. Zhao, C. Xu, 2007. "Three-dimensional two-phase mass transport model for direct methanol fuel cells". *Electrochimica Acta*, 53(2): 853-862.

Zhao, T.S., C. Xu, R. Chen, W.W. Yang, 2009. "Mass transport phenomena in direct methanol fuel cells". *Progress in Energy and Combustion Science*, 35(3): 275-292.

Zignani, S.C., E.R. Gonzalez, V. Baglio, S. Siracusano, A.S. Aricò, 2012. "Investigation of a Pt 3 Sn / C Electro-Catalyst in a Direct Ethanol Fuel Cell Operating at Low Temperatures for Portable Applications", 7: 3155-3166.