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A transient multi-scale model for direct methanol fuel cells

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ABSTRACT

The DMFC is a promising option for backup power systems and for the power supply of portable devices. However, from the modeling point of view liquid-feed DMFC are challenging systems due to the complex electrochemistry, the inherent two-phase transport and the effect of methanol crossover. In this paper we present a physical 1D cell model to describe the relevant processes for DMFC performance ranging from electrochemistry on the surface of the catalyst up to transport on the cell level. A two-phase flow model is implemented describing the transport in gas diffusion layer and catalyst layer at the anode side. Electrochemistry is described by elementary steps for the reactions occurring at anode and cathode, including adsorbed intermediate species on the platinum and ruthenium surfaces. Furthermore, a detailed membrane model including methanol crossover is employed. The model is validated using polarization curves, methanol crossover measurements and impedance spectra. It permits to analyze both steady-state and transient behavior with a high level of predictive capabilities. Steady-state simulations are used to investigate the open circuit voltage as well as the overpotentials of anode, cathode and electrolyte. Finally, the transient behavior after current interruption is studied in detail.

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1. INTRODUCTION

Direct methanol fuel cell (DMFC) technology is promising as a power source for portable and uninterruptible power supply applications, due to the direct use of a high energy density liquid fuel, quick recharging by refilling and low operating temperature [1,2].

However, the use of a methanol/water liquid mixture as fuel, as required by electrochemistry, increases the complexity of the system and entails some additional challenges:

- a complex two-phase and multi-component flow has to be managed at the anode side;
- the methanol oxidation is a complex multi-step mechanism leading to a strong CO poisoning of the platinum catalyst: to improve the capability of methanol oxidation platinum-ruthenium catalysts are used for DMFC anodes;
- methanol permeates through the membrane and the resulting methanol oxidation at the cathode side leads to waste of fuel and significantly affects cathode potential, forming a so called mixed potential.

In addition, other technical issues must still be overcome to enter into the market, among which is the severe performance degradation over operation time. DMFC performance losses show a permanent and a temporary contribution at both anode and cathode [3–5]. The former is due to irreversible degradation mechanisms, such as platinum dissolution and agglomeration at the cathode, while the latter is partially recovered by utilizing appropriate operating strategies [6]. Usually these strategies consist of a period of continuous operation interspersed by a sequence of OCV and/or cathode air feeding interruption.

Current research activities aim at studying DMFC transient behavior to improve and consolidate the understanding of system operation and to set the basis for reducing DMFC degradation. Due to the complex and nonlinearly-coupled processes taking place in DMFCs, modeling and simulation are highly useful tools [7–12].

Wang and Wang [7] presented a two-phase model, taking into account the effect of methanol crossover, but considering only global reactions for methanol oxidation reaction (MOR) and oxygen reduction reaction, i.e., did not take into account the effect of CO poisoning.

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Nomenclature

A_k^{V}	Volume-specific surface area corresponding to reaction k ($\mathrm{m^2\,m^{-3}}$)
c_i	Concentration of species i in a bulk phase ($\mathrm{mol\,m^{-3}}$)
C_{dl}	Area-specific double layer capacitance ($\mathrm{F\,m^2}$)
d_i	Drag coefficient of species i
d_{p}	Average particle diameter (m)
D_i^p	Diffusion coefficient of species i in phase p ($\mathrm{m^2\,s^{-1}}$)
E	Cell voltage (V)
EW	Equivalent weight of membrane ($\mathrm{kg\,eq^{-1}}$)
$E_{\mathrm{f}}^{\mathrm{act}}$	Activation energy of forward and reverse reactions ($\mathrm{J\,mol^{-1}}$)
f_σ	Ratio of ionic conductivity of porous over bulk electrolyte
F	Faraday's constant ($\mathrm{C\,mol^{-1}}$)
H	Henry's constant ($\mathrm{mol\,m^{-3}\,Pa}$)
i	Current density ($\mathrm{A\,m^{-2}}$)
$j_i^{\mathrm{l,\,diff}}$	Mass diffusion flux of species i in liquid phase ($\mathrm{kg\,m^{-2}\,s^{-1}}$)
$j_i^{\mathrm{l,\,conv}}$	Mass convection flux of species i in liquid phase ($\mathrm{kg\,m^{-2}\,s^{-1}}$)
$J_i^{\mathrm{g,\,diff}}$	Molar diffusion flux of species i in gas phase ($\mathrm{mol\,m^{-2}\,s^{-1}}$)
$J_i^{\mathrm{g,\,conv}}$	Molar convection flux of species i in gas phase ($\mathrm{mol\,m^{-2}\,s^{-1}}$)
k^p	Permeability of phase p ($\mathrm{m^2}$)
k_{abs}	Absolute permeability ($\mathrm{m^2}$)
$k_{\mathrm{rel}}^{\mathrm{p}}$	Relative permeability of phase p
l_n^{V}	Volume-specific three-phase boundary length corresponding to reaction n ($\mathrm{m\,m^{-3}}$)
La	Thickness of anode (GDL + CL) (m)
Lc	Thickness of cathode (GDL + CL) (m)
Lm	Thickness of membrane (m)
M_i	Molar mass of species i ($\mathrm{kg\,mol^{-1}}$)
p^{c}	Capillary pressure (Pa)
p^{g}	Gas pressure (Pa)
p_i^{g}	Partial pressure of species i in gas phase (Pa)
p^{l}	Liquid pressure (Pa)
$\bar{p}^p$	Pressure of phase p averaged over channel length (Pa)
R	Ideal gas constant ($\mathrm{J\,K^{-1}\,mol^{-1}}$)
s	Liquid saturation
$\dot{s}_i^k$	Chemical production rate of species i in reaction k (in units of $\mathrm{m^{-2}}$ for two-phase reactions and $\mathrm{m^{-1}}$ for three-phase reactions) ($\mathrm{mol\,m^{-2}\,s^{-1}}$) ($\mathrm{mol\,m^{-1}\,s^{-1}}$)
$\dot{s}_i^{\mathrm{cond}}$	Production rate of species i due to condensation ($\mathrm{mol\,m^{-2}\,s^{-1}}$)
$\dot{s}_{\mathrm{electron},m}$	Electron production rate in reaction m (in units of $\mathrm{m^{-2}}$ for two-phase reactions and $\mathrm{m^{-1}}$ for three-phase reactions) ($\mathrm{mol\,m^{-2}\,s^{-1}}$) ($\mathrm{mol\,m^{-1}\,s^{-1}}$)
t	Time (s)
T	Temperature (K)
v^{conv}	Convection velocity in liquid phase ($\mathrm{m\,s^{-1}}$)
$\bar{V}_{\mathrm{H2O}}$	Molar volume of water ($\mathrm{mol\,m^{-3}}$)
$\bar{V}_{\mathrm{mem}}$	Molar volume of the dry membrane ($\mathrm{mol\,m^{-3}}$)
x_i^p	Mole fraction of species i in phase p
z	Number of electrons transferred in charge-transfer step
α	Symmetry factor of charge transfer reaction
α_w	Water exchange coefficient ($\mathrm{mol\,m^{-2}\,s^{-1}}$)
α_m	Methanol exchange coefficient ($\mathrm{mol\,m^{-2}\,s^{-1}}$)
Γ_i	Site density of surface i ($\mathrm{mol\,m^{-2}}$)
ΔH	Reaction enthalpy ($\mathrm{J\,mol^{-1}}$)
ΔS	Reaction entropy ($\mathrm{J\,K^{-1}\,mol^{-1}}$)
$\Delta\phi$	Electric potential difference between electrode and electrolyte (V)
ε	Porosity
ε_i	Volume fraction of phase i
ϕ	Electric potential (V)
μ^g	Gas-phase viscosity ($\mathrm{kg\,m^{-1}\,s^{-1}}$)
μ^l	Liquid-phase viscosity ($\mathrm{kg\,m^{-1}\,s^{-1}}$)
ρ_i^l	Density of species i ($\mathrm{kg\,m^{-3}}$)
σ_{mem}	membrane conductivity ($\mathrm{S\,m^{-1}}$)
τ	Tortuosity of porous electrode

Siebke et al. [8] developed a DMFC model, in which a multi-step mechanism for the MOR is considered at the anode side while at the cathode MOR and oxygen reduction reaction (ORR) are modeled using Tafel equations. The model was used to investigate the limiting processes at high current densities depending on the operating conditions.

Casalegno et al. considered a 1D + 1D steady-state model including two-phase transport, where the reaction kinetics of MOR and ORR is given by Tafel equations and validated the model for a wide range of operating conditions and with diffusion layer configurations [9].

Gerteisen [10] presented a multi-step model for MOR and ORR including oxygen bleeding to remove the CO poisoning at the cathode. The model was used to discuss transient effects, e.g., the dynamics of CO poisoning after current interruption. However, the model did not include two-phase transport.

Kulikovsky [11] developed an analytical model for cathode mixed potential based on Butler-Volmer kinetics of the ORR.

From the modeling point of view, only very limited work has been carried out concerning the simulation and experimental validation of both DMFC steady-state and dynamic behavior, that is fundamental to couple performance and degradation models [13].

Hence, the aim of this work is to develop a physical DMFC model which is capable of describing the performance of DMFC during steady-state as well as transient operation. In this paper we first present a detailed cell model based on the in-house modeling framework DENIS [14,15] which provides several models for high and low temperature fuel cells as well as different types of batteries. This framework has been complemented by the DMFC model presented in this paper by including the relevant mechanisms mentioned before, i.e., two-phase-flow, a multi-step mechanism for the methanol oxidation as well as methanol crossover and multi-step MOR and ORR at the cathode. All implemented model equations are presented in the first part of this paper. Next, we show validation of the model with respect to different experimental measurements, i.e., polarization curves, methanol crossover measurements and electrochemical impedance spectra. Finally, after validation, the relevance of the different mechanisms on the cell performance and on the transient behavior of the cell is discussed. In particular, the effects of current interruption are investigated.

2. MODEL

In the following we describe the developed DMFC model including all model equations and parameters. A 1D continuum approach is used to model the Membrane Electrode Assembly (MEA). The model is isothermal and is composed of several sub-models for the different components (gas diffusion layers (GDLs), catalyst layers (CLs) and membrane (MEM)). The different domains

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