



Short communication

An analytical model of NafionTM membrane humidifier for proton exchange membrane fuel cells

Sehkyu Park*, In-Hwan Oh

Fuel Cell Research Center, Korea Institute of Science and Technology, 39-1 Hawolgok-dong, Seongbuk-gu, Seoul 136-791, Republic of Korea

ARTICLE INFO

Article history:

Received 4 December 2008

Accepted 5 December 2008

Available online 11 December 2008

Keywords:

Analytical model
NafionTM membrane humidifier
Relative humidity
PEM fuel cells

ABSTRACT

This paper introduced a one-dimensional analytical model to quantitatively examine the humidifying capacity of a NafionTM membrane humidifier. Water permeability for the NafionTM membrane was calculated, depending on the thickness of the NafionTM membrane. Relative humidity for a carrier gas passed through the NafionTM membrane humidifier was simulated at various gas flow rates, which showed good agreement with experimental data. Simulations were also conducted to predict humidity levels as a function of length and height of the gas flow channel. This analytical model can be used in future work to properly design NafionTM membrane humidifiers for use in PEM fuel cell systems.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Proton exchange membrane (PEM) fuel cells are highly efficient energy-conversion devices for automotive and stationary applications. Typically, the humidified fuel and oxidant are introduced to the anode and the cathode compartments in order to make the membrane fully hydrated in a wide current range [1–3].

Past research has focused on developing various humidifying methods to effectively supply humid reactants into the PEM fuel cells [4–9]. Reid [4] attempted to humidify a reactant by passing it through a heated water reservoir, while Nguyen and White [5] suggested direct water spraying into the gas stream. Chow and Wozniczka [6] developed a membrane humidifier capable of serving water vapor to a reactant. As illustrated in Fig. 1, the membrane is sandwiched between the gas flow channel (i.e., permeate side) and the water (or humid gas) flow channel (i.e., feed side). Water permeates through the membrane and evaporates into the gas stream due to a lower partial pressure exerted on the permeate side of the membrane [10].

Recent simulation studies [11–14] yielded a deeper understanding of how water moves into a carrier gas through the NafionTM membrane for various operating conditions: gas flow rate, gas or water temperature, water pressure. The models in these studies were proposed to calculate water content in a carrier gas at the

outlet, in terms of NafionTM membrane humidifier performance. Although these models contribute to the analysis and prediction of water transport through the NafionTM membrane in a humidifier, they are difficult to apply in practice because of their complex forms. Hence, a simplified model is necessary and helpful to evaluate humidification using the NafionTM membrane for PEM fuel cell applications. In this study, a one-dimensional analytical expression was developed. Water permeability was calculated based on previous experimental results [9]. The relative humidity for a carrier gas passed through the NafionTM membrane humidifier at various flow rates was predicted using an analytical model and validated by comparing with experimental data. The effects of the dimensions of the gas flow channel on the humidifying capacity of the NafionTM membrane humidifier were also examined.

2. Mathematical model

The mass flux of water from the water flow channel to the gas flow channel through the membrane in Fig. 1 is expressed as [10,15]

$$N_w^{\text{mem}} = k_w(x_w\gamma_w p_{w,0} - y_w P) \quad (1)$$

where k_w is the water permeability, x_w is the mole fraction of the water in liquid phase, γ_w is the activity coefficient of the water, $p_{w,0}$ is the saturated pressure of the water at a given temperature, y_w is the mole fraction of the water in gas phase, and P is the total pressure. Based on the assumptions that (i) the gases behave as ideal ones, (ii) the membrane humidifier is isothermal, (iii) the total pressure remains constant (i.e., ambient pressure), (iv) the partial pressure of water vapor changes only in the z -direction, (v) the water permeability is constant, and (vi) the gas flow channel

* Corresponding author. Present address: Center for Electrochemical Engineering, Department of Chemical Engineering, University of South Carolina, 301 Main St. Swearingen Engineering Center, Columbia, SC 29208, USA. Tel.: +1 803 576 5634; fax: +1 803 777 8265.

E-mail address: park46@engr.sc.edu (S. Park).

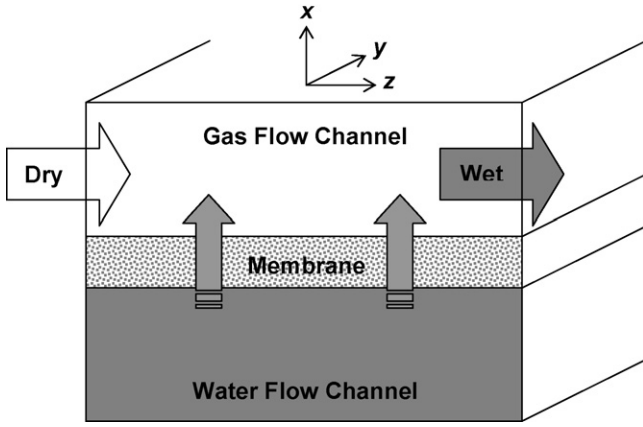


Fig. 1. Schematic diagram of a membrane humidifier.

is straight, the mass balance on water vapor along the gas flow channel can be established as follows:

$$N_w|_z WH - N_w|_{z+\Delta z} WH + k_w(p_{w,0} - p_w)W\Delta z = 0 \quad (2)$$

where W is the width of the gas flow channel, H is the height of the gas flow channel, and Δz is the thickness of an intersection of the gas flow channel. Dividing Eq. (2) by $WH\Delta z$ and taking the limit as Δz approaches zero gives

$$\frac{dN_w}{dz} = \frac{k_w}{H}(p_{w,0} - p_w) \quad (3)$$

The partial pressure of water vapor is a function of both x and z . However, the partial pressure of water vapor can be considered virtually as a function of z alone since the velocity profile of a carrier gas is not significantly affected by the evaporation across cross-section of the gas flow channel [16]. When the flow in the gas channel is dominated by convection (i.e., $Pe = vL/D_{w-g} \gg 1$), the constitute equation for water flux in the gas flow channel is

$$N_w = -cD_{w-g} \frac{dx_w}{dz} + x_w(N_w + N_g) \approx c_w v \quad (4)$$

$$\text{with } c_w = \frac{p_w}{RT} \quad (5)$$

where D_{w-g} is the water/gas binary diffusion coefficient, N_g is the gas flux, c_w is the water concentration, v is the gas flow rate, R is the gas constant, and T is the temperature. Substituting Eqs. (4) and (5) into Eq. (3) yields

$$\frac{dp_w}{dz} = \frac{k_w RT}{vH}(p_{w,0} - p_w) \quad (6)$$

If the partial pressure of the water at the gas flow channel inlet p_w^{inlet} is known, Eq. (6) can be solved analytically as follows:

$$\frac{p_w}{p_{w,0}} = 1 - \exp\left[-\left(\frac{k_w RT}{vH}\right)z\right] \left(1 - \frac{p_w^{\text{inlet}}}{p_{w,0}}\right) \quad (7)$$

3. Results and discussion

3.1. Determination of water permeability

The relative humidity H_R is defined as

$$H_R = \frac{p_w}{p_{w,0}} \times 100 \quad (8)$$

As shown in Fig. 2, the relative humidity H_R measured at various air flow rates was plotted in the plane of $-\ln(1 - p_w/p_{w,0})$ versus v^{-1} , to calculate water permeability k_w for a NafionTM membrane with different thicknesses. The experiment performed to obtain the

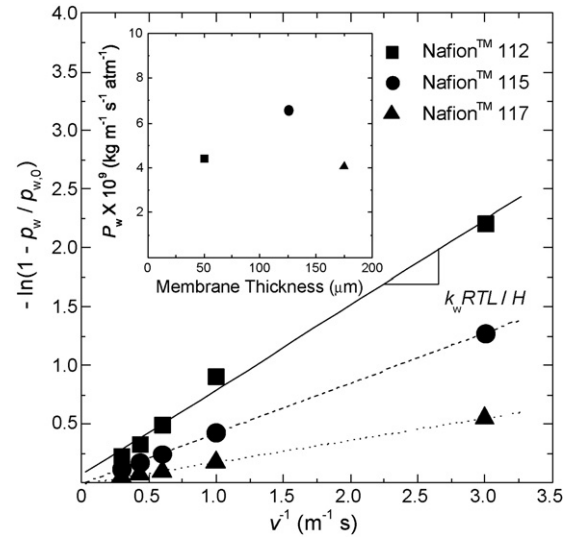


Fig. 2. Determination of the water permeability for NafionTM membranes. (inset) The water permeability coefficient for a NafionTM membrane.

relative humidity data in Fig. 2 is fully described in [9]. In Fig. 2, the value of k_w for the NafionTM membrane is determined by modifying Eq. (7). i.e.,

$$-\ln\left(1 - \frac{p_w}{p_{w,0}}\right) = \frac{k_w R T L}{vH} \quad (9)$$

where L is the length of gas flow channel in the NafionTM membrane humidifier ($L = 0.297$ m). The values of k_w calculated from Eq. (9) are 8.9×10^{-5} , 5.3×10^{-5} , and 2.3×10^{-5} $\text{kg m}^{-2} \text{s}^{-1} \text{atm}^{-1}$ for NafionTM 112, 115, and 117, respectively. These results indicate that values of k_w for the NafionTM membrane are strongly related to the thickness.

The process of membrane humidification includes the diffusion of water through the membrane and interfacial mass-transfer, which includes sorption into the membrane on the feed side and desorption into a carrier gas on the permeate side [10,11,17]. If the interfacial mass-transfer is dominant in the membrane humidification, the water permeability is highly related to gas flow rate. This is mainly because the thickness of the boundary layer at the permeate side (i.e., the interface between a carrier gas and the membrane) is largely affected by gas flow rate, when the boundary layer at the feed side is assumed to be negligibly thin. On the other hand, if the diffusion through the membrane is dominant in humidification, the value of k_w is inversely proportional to thickness of the membrane.

The permeability coefficient of water across a membrane P_w is the product of water permeability k_w and thickness of a membrane δ_{mem} [10,15]. As seen in Fig. 2, the values of P_w for a NafionTM membrane with different thicknesses are between 4.0 and 6.6×10^{-9} $\text{kg m}^{-1} \text{s}^{-1} \text{atm}^{-1}$ (see the inset). The inconsistency of P_w values may originate primarily from the theoretical assumption that the mass flux of water vapor is expressed as $k_w(p_{w,0} - p_w)$ where k_w is not a function of position but constant and p_w is a function of z alone. This issue will be addressed in future work. However, even if the values of P_w vary somewhat, it is clear that diffusion is the dominant process in determining k_w , since k_w is not appreciably affected by gas flow rate.

3.2. Effect of gas flow rate

Fig. 3 displays the values of H_R for a carrier gas passed through a NafionTM membrane humidifier at various flow rates using Eq. (7). The simulations were performed at 60°C. The values of k_w

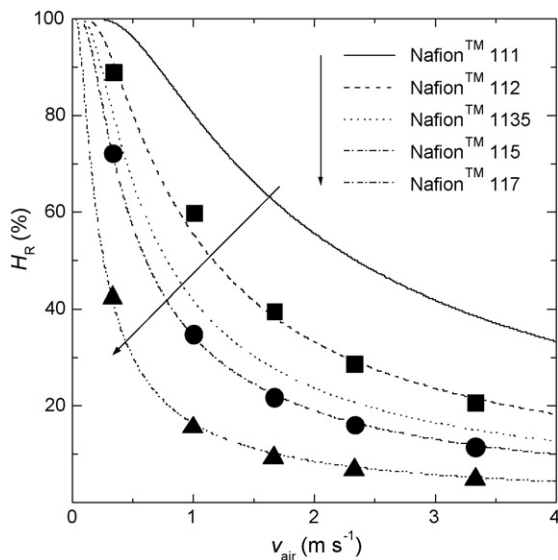


Fig. 3. Relative humidity for a carrier gas passed through a Nafion™ membrane humidifier as a function of gas flow rate.

for Nafion™ 111 ($\approx 25 \mu\text{m}$) and 1135 ($\approx 87 \mu\text{m}$) were calculated as 2.0×10^{-4} and $6.7 \times 10^{-5} \text{ kg m}^{-2} \text{ s}^{-1} \text{ atm}^{-1}$, which were calculated using $P_w = 5.0 \times 10^{-9} \text{ kg m}^{-1} \text{ s}^{-1} \text{ atm}^{-1}$, and the values of L and H were 0.297 m and 1 mm. Our previous experimental data are also shown in Fig. 3 [9]. The simulation results shown in the figure agree with the values of H_R measured at various air flow rates. When the gas flow rate ν increases, H_R values for a carrier gas decay drastically at low flow rates, especially for a thicker Nafion™ membrane. H_R values at $\nu = 0.333 \text{ m s}^{-1}$ were 99.2% for Nafion™ 111, 88.6% for Nafion™ 112, 80.2% for Nafion™ 1135, 72.3% for Nafion™ 115, and 43.0% for Nafion™ 117, respectively. At high flow rates, H_R decreases slowly, showing smaller differences between Nafion™ membranes. These results imply that a carrier gas is not sufficiently humidified at high flow rates due to short residence time in the membrane humidifier, even if a thinner Nafion™ membrane is used.

3.3. Effect of gas flow channel length

In a membrane humidifier, a carrier gas supplied into the gas flow channel is humidified when it moves in the z -direction, as portrayed in Fig. 1. Hence, it is very important to predict the humidifying capacity of Nafion™ membranes as a function of length of the gas flow channel, which is coupled with the volume of the Nafion™ membrane humidifier. Fig. 4(a) delineates the values of H_R along the gas flow channel for a carrier gas passed through Nafion™ membrane humidifier. The simulations were conducted at 60°C , and the values of ν and H were 0.333 m s^{-1} and 1 mm. As represented in Fig. 4(a), the lengths of the gas flow channel necessary to obtain H_R of 80% for a carrier gas were 0.10, 0.22, 0.29, 0.37, and 0.85 m for Nafion™ 111, 112, 1135, 115, and 117, respectively.

A carrier gas introduced into a Nafion™ membrane humidifier may contain water vapor, relying on methods such as the electrolysis and steam reforming process to produce reactants. Fig. 4(b) specifies the values of H_R along the gas flow channel using different Nafion™ membranes at $H_{R,\text{inlet}}$ of 40%. Comparing the profiles of H_R for different Nafion™ membranes in Fig. 4(b), the pattern of H_R values is similar to that shown in Fig. 4(a). However, the gas flow channel lengths to reach H_R of 80% are shorter by ca. 60% than those with vapor-free gas at the inlet (i.e., Fig. 4(a)). Fig. 5 depicts the values of H_R as a function of length of the gas flow channel in Nafion™ 112 membrane humidifier, when the values of H_R at the inlet are 0, 20, 40, 60, and 80%, respectively. Note that the gradients

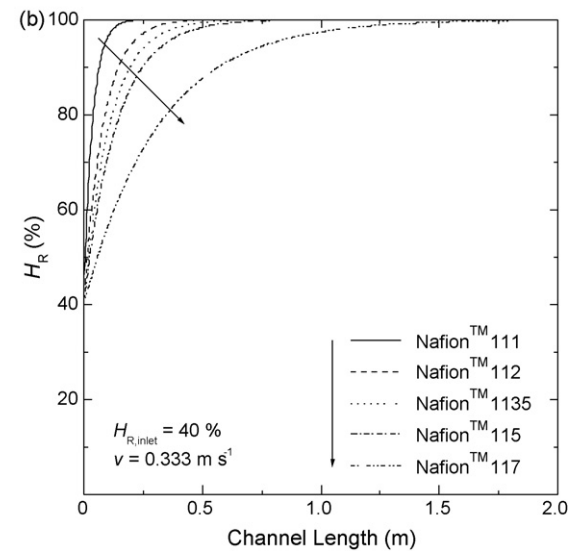
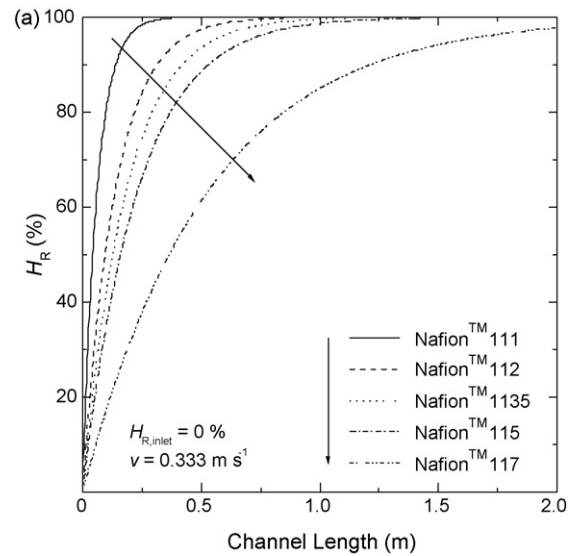


Fig. 4. Relative humidity for a carrier gas passed through a Nafion™ membrane humidifier as a function of gas flow channel length at (a) $H_{R,\text{inlet}} = 0\%$ and (b) $H_{R,\text{inlet}} = 40\%$.

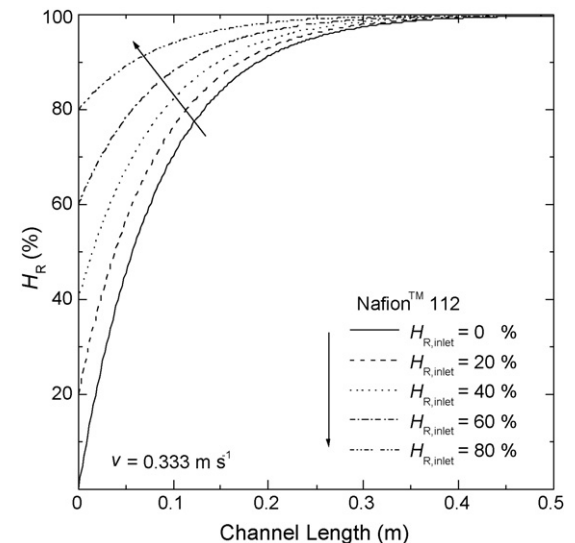


Fig. 5. Relative humidity for a carrier gas along the gas flow channel at various $H_{R,\text{inlet}}$ for Nafion™ 112.

Table 1

Maximum gas flow rates to obtain H_R of 80% using Nafion™ membrane humidifiers and the currents generated under stoichiometry with $\lambda_{\text{air}} = 3$ (operating temperature in Nafion™ membrane humidifiers and a PEM fuel cell is 60 °C).

Membrane	v_{max} (m s ⁻¹)	I_{air} (A)
Nafion™ 111	1.009	68.6
Nafion™ 112	0.447	30.4
Nafion™ 1135	0.336	22.8
Nafion™ 115	0.266	18.1
Nafion™ 117	0.116	7.9

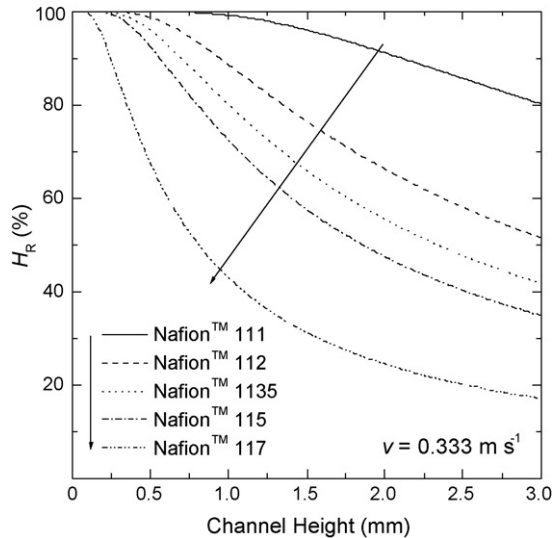


Fig. 6. Relative humidity for a carrier gas passed through a Nafion™ membrane humidifier as a function of gas flow channel height.

of H_R near the inlet decreases with increasing $H_{R,\text{inlet}}$, whereas the lengths of the gas flow channel needed to reach H_R of 100% decrease with higher $H_{R,\text{inlet}}$.

According to Wilkinson et al. [18], relative humidity of 80% for an oxidant introduced to the cathode inlet is high enough to sufficiently maintain ionic conductivity of the membrane. Assuming that the stoichiometry of the fully humidified hydrogen is sufficiently high at the anode compartment in a PEM fuel cell ($\lambda_{\text{H}_2} \gg 1$), the maximum gas flow rate v_{max} to reach H_R of 80% for a carrier gas using Nafion™ membrane humidifier ($L = 0.297$ m) and the current generated from a PEM fuel cell under constant stoichiometry with $\lambda_{\text{air}} = 3$ are summarized in Table 1. When air is used as an oxidant, the current generated under constant stoichiometry is calculated as follows [19]

$$I_{\text{air}} = \frac{4v_{\text{max}}A_{\text{ch}}FP}{RT\lambda_{\text{air}}} \quad (10)$$

where A_{ch} is the cross-section area of the gas flow channel at the cathode compartment, F is the Faraday constant, P is the total pressure in a PEM fuel cell, respectively. As listed in Table 1, the value of I_{air} for Nafion™ 111 is 8.7 times higher than that for Nafion™ 117. Using Eqs. (7) and (10), the minimum length of the gas flow channel in the Nafion™ membrane humidifier for demanding maximum current can be quantitatively estimated.

3.4. Effect of gas flow channel height

Fig. 6 exhibits the values of H_R for a carrier gas passed through a Nafion™ membrane humidifier with different gas flow channel

heights using Eq. (7). The simulations were performed at 60 °C, and the values of v and L were 0.333 m s⁻¹ and 0.297 m, respectively. The value of H_R at the outlet of the Nafion™ membrane humidifier remains near 100% and then decreases significantly as gas flow channel height increases, depending on the thickness of the Nafion™ membrane. Interestingly, the value of H_R for a carrier gas passed through the Nafion™ 111 membrane humidifier is higher than 99%, when the gas flow channel height ranges from 0 to 1 mm. As illustrated in Fig. 6, when the thickness of Nafion™ membrane varies between 25 and 175 μm, the value of H_R from the Nafion™ membrane humidifier with $H = 2$ mm drops from 91.3% to 24.5%. The simulations in Fig. 4(a) and 6 clarify that in the case of Nafion™ 111, the length and height of the gas flow channel necessary to reach H_R of 80% for a carrier gas at $v = 0.333$ m s⁻¹ are ca. 8.5 times smaller and larger than those in the case of Nafion™ 117, respectively. That is, the minimum volume of the gas flow channel for Nafion™ 111 to operate a fuel cell at a given current without a significant drop in ionic conductivity of the membrane is ca. 8.5 times smaller than that for Nafion™ 117.

4. Conclusion

The results of this study indicated that a thinner Nafion™ membrane leads to higher relative humidity for a carrier gas, since water permeability depends heavily on the thickness of a Nafion™ membrane. Relative humidity for a carrier gas passed through a Nafion™ membrane humidifier was calculated using an analytical expression along the gas flow channel, as a function of gas flow rate, length, and height of the gas flow channel. This analytical model can be utilized to effectively design Nafion™ membrane humidifier for PEM fuel cells.

Acknowledgments

The authors thank Dr. Jang-ho Jo for his comment and help.

References

- [1] T.F. Fuller, J. Newman, J. Electrochem. Soc. 139 (1992) 1332–1337.
- [2] T.E. Springer, M.S. Wilson, S. Gottesfeld, J. Electrochem. Soc. 140 (1993) 3513–3526.
- [3] F. Barbir, PEM Fuel Cells, Elsevier Academic Press, Burlington, 2005.
- [4] P.L. Reid, U.S. Patent No. 4,759,882 (1988).
- [5] T.V. Nguyen, R.E. White, J. Electrochem. Soc. 140 (1993) 2178–2186.
- [6] C.Y. Chow, B.W. Wozniczka, U.S. Patent No. 5,382,478 (1995).
- [7] K.H. Choi, D.J. Park, Y.W. Rho, Y.T. Kho, T.H. Lee, J. Power Sources 74 (1998) 146–150.
- [8] P. Sridhar, R. Perumal, N. Rajalakshmi, M. Raja, K.S. Dhathatheryan, J. Power Sources 101 (2001) 72–78.
- [9] S. Park, E.A. Cho, I.-H. Oh, Korean J. Chem. Eng. 22 (2005) 877–881.
- [10] M. Mulder, Basic Principles of Membrane Technology, Kluwer Academic Publishers, Dordrecht, 1996.
- [11] P.W. Majsztrik, M.B. Satterfield, A.B. Bocarsly, J.B. Benziger, J. Membr. Sci. 301 (2007) 93–106.
- [12] P. Cave, W. Mérida, J. Power Sources 175 (2008) 408–416.
- [13] D. Chen, W. Li, H. Peng, J. Power Sources 180 (2008) 461–467.
- [14] R. Huizing, M. Fowler, W. Mérida, J. Dean, J. Power Sources 180 (2008) 265–275.
- [15] W.L. McCabe, J.C. Smith, P. Harriott, Unit Operations of Chemical Engineering, 5th ed., McGraw Hill, Inc., New York, 1993.
- [16] R.B. Bird, W.E. Stewart, E.N. Lightfoot, Transport Phenomena, John Wiley & sons, New York, 1960.
- [17] S. Ge, X. Li, B. Yi, I.-M. Hsing, J. Electrochem. Soc. 152 (2005) A1149–A1157.
- [18] D.P. Wilkinson, H.H. Voss, K. Prater, J. Power Sources 49 (1994) 117–127.
- [19] J. Larminie, A. Dicks, Fuel Cell Systems Explained, 2nd ed., John Wiley & sons, West Sussex, England, 2003.