Comparing predictions of PEM fuel cell behavior using Maxwell–Stefan and CFD approximation equations

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A B S T R A C T

This study examines the accuracy of solving the multi-component equations for a Proton Exchange Membrane Fuel Cell (PEMFC) by using a Computational Fluid Dynamics (CFD) technique. This technique uses an approximated multi-component (AMC) model with a correction term that guarantees the overall mass balance. Accuracy is assessed by comparing the species concentration computed with the Maxwell–Stefan and the corrected AMC models. This comparison is important because the structure of some CFD programs does not permit the direct use of the Maxwell–Stefan equations and this leads to confusion in the literature and to implications that CFD predictions are not accurate because a different set of transport equations and mixture diffusion coefficients are used. Here, it is shown that this controversy is ill-founded because the maximum error between the two models is less than 5%. Thus, the use of the corrected AMC model is appropriate for PEMFC applications.

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1. Introduction

Computational Fluid Dynamics (CFD) can be a valuable technique for generating two-dimensional and three-dimensional geometric representations of Proton Exchange Membrane Fuel Cells (PEMFC) and for solving the resulting transport equations (i.e., models) in order to understand the physical and chemical processes inside the cell (Shimpalee, Lee, & Van Zee, 2006). Often, these systems involve the coupled mass, momentum, and energy transport of more than two species in complex geometries and the desire for high resolution of the resulting profiles with industrially relevant dimensions requires 10–20 million volume elements or computational cells (Shimpalee, 2005). These multi-component transport models could be formulated by using the Maxwell–Stefan equations but two issues arise. First, the use of the Maxwell–Stefan equations for multi-component diffusion leads to a numerical-solution matrix structure (whether one uses a Jacobian or a Simplex-type solution approach) for the set of equations that depends on the number of equations (i.e., species) in the set and this lack of structure can produce large non-efficient storage and computational time requirements. Secondly and perhaps more importantly, CFD codes are typically written on a mass basis which is not easily translated to the Maxwell–Stefan equations for describing species transport. That is, although the Maxwell–Stefan equations can be expressed as mass fraction gradient (Sutton & Gnoffo, 1998), the resulting expressions are either not completely on a mass basis (i.e., mass fluxes and mass fraction) or they can result in a complicated expression which does not have an analog to its counterpart on a mole basis. Therefore, it is common to use approximation methods which results in system of equations easier to solve.

One approach for calculating the profiles resulting from a multi-component diffusion model is to use mass conservation equations with Fick’s law and an effective diffusion coefficient for the species in the mixture. However, there is a problem with this approach in that global mass conservation is not guaranteed. This has led researchers of different fields and applications to compare Fickian-based model predictions using effective diffusion coefficients for multi-component transport with those of Maxwell–Stefan models (Banat, Abu Al-Rub, Jumah, & Shannag, 1999; Sutton & Gnoffo, 1998; Suwanwarangkul et al., 2003) and to develop alternatives to the CFD correction term approach. For example, Banat et al. (1999) compared the Fickian-based model from Udriot, Araque, & von Stockar (1994) with a Maxwell–Stefan based model for a membrane distillation process. The model predictions based on the Maxwell–Stefan equations were closer to the experimental data than the Fickian-based model. Although the Maxwell–Stefan model includes improvements on the description of the interface conditions, the authors also attribute the better fit to the coupling interactions when the Maxwell–Stefan equations are used.

Based on the previous discussion it is known that the Maxwell–Stefan equations provide a better description than the...
Nomenclature

\[ c \] \text{ total molar density of the solution (mol/cm}^3) \\
\[ c_\alpha \] \text{ molar density of species } \alpha \text{ (mol/cm}^3) \\
\[ c_\alpha \] \text{ integration constant of species } \alpha \\
\[ D_{\alpha m} \] \text{ free-stream diffusion coefficient of species } \alpha \text{ in the mixture (cm}^2/s) \\
\[ D_{\alpha \beta} \] \text{ free-stream binary diffusion coefficient for species } \alpha \text{ and } \beta \text{ (cm}^2/s) \\
\[ p_{\alpha m} \] \text{ effective diffusion coefficient of species } \alpha \text{ in the mixture (cm}^2/s) \\
\[ p_{\alpha \beta} \] \text{ effective binary diffusion coefficient for species } \alpha \text{ and } \beta \text{ (cm}^2/s) \\
\[ F \] \text{ Faraday’s constant (96,487 C/equiv) } \\
\[ i \] \text{ superficial current density (A/cm}^2) \\
\[ J_{\alpha} \] \text{ molar flux of species } \alpha \text{ relative to } v^1 \\
\[ M \] \text{ mean molecular weight (g/mol) } \\
\[ M_\alpha \] \text{ molecular weight of species } \alpha \text{ (g/mol) } \\
\[ N_{\alpha} \] \text{ correction molar flux (mol/(cm}^2s)) \\
\[ N_\alpha \] \text{ total molar flux (mol/(cm}^2s)) \\
\[ N_{\alpha z} \] \text{ component of molar flux for species } \alpha \text{ (mol/(cm}^2s)) \\
\[ \rho \] \text{ pressure (kPa) } \\
\[ r_{\text{sat} H_2O} \] \text{ saturation pressure of water (kPa) } \\
\[ r^\alpha \] \text{ reaction rate of species } \alpha \text{ by homogeneous reaction (g/cm}^3s) \\
\[ r'_{\alpha} \] \text{ reaction rate of species } \alpha \text{ by heterogeneous reaction (g/cm}^3s) \\
\[ R \] \text{ universal gas constant (8314 (cm}^3 kPa)/(mol K)) \\
\[ RH \] \text{ relative humidity (g water/g air) } \\
\[ t \] \text{ time (s) } \\
\[ T \] \text{ absolute temperature (K) } \\
\[ v^\alpha \] \text{ molar-averaged velocity (cm/s) } \\
\[ v_c^\alpha \] \text{ correction molar-averaged velocity (cm/s) } \\
\[ Y_\alpha \] \text{ molar fraction of species } \alpha \\
\[ z \] \text{ coordinate direction normal to the anode flow channel (cm) } \\
\[ \alpha \] \text{ species } \alpha \\
\[ \beta \] \text{ species } \beta \\
\[ \delta \] \text{ thickness (cm) } \\
\[ \varepsilon \] \text{ porosity } \\
\[ \rho \] \text{ total mass density of the solution (g/cm}^3) \\
\[ \rho_\alpha \] \text{ mass density of species } \alpha \text{ (g/cm}^3) \\
\[ o_\alpha \] \text{ mass fraction of species } \alpha \\
\[ \xi_{\text{H}2O} \] \text{ electro-osmotic drag coefficient of water}

Subscripts

\[ A \] \text{ ABL, anode backing layer } \\
\[ c \] \text{ indicator for correction term } \\
\[ C \] \text{ CBL, cathode backing layer } \\
\[ H_2 \] \text{ hydrogen } \\
\[ H_2O \] \text{ water } \\
\[ N_2 \] \text{ nitrogen } \\
\[ O_2 \] \text{ oxygen } \\
\[ \alpha \] \text{ species } \alpha \\
\[ \beta \] \text{ species } \beta \\
\[ A \] \text{ ABL, anode backing layer } \\
\[ C \] \text{ CBL, cathode backing layer } \\
\[ M \] \text{ membrane }

Greek letters

\[ \alpha \] \text{ species } \alpha \\
\[ \beta \] \text{ species } \beta \\
\[ \delta \] \text{ thickness (cm) } \\
\[ \varepsilon \] \text{ porosity } \\
\[ \rho \] \text{ total mass density of the solution (g/cm}^3) \\
\[ \rho_\alpha \] \text{ mass density of species } \alpha \text{ (g/cm}^3) \\
\[ o_\alpha \] \text{ mass fraction of species } \alpha \\
\[ \xi_{\text{H}2O} \] \text{ electro-osmotic drag coefficient of water}

2. Model description

To compare the accuracy of the AMC equations, we use a model that describes the species concentration in the anode backing layer (ABL) and in the cathode backing layer (CBL). It is important to note that comparisons are being made based on the gas transport in the backing layers. Consequently, the membrane model is not within the focus of this study. Furthermore, constitutive equations for condensation, evaporation, and heat transfer are not required for this comparison of accuracy. Fig. 1 shows a schematic diagram of the PEMFC illustrating the frame of reference and the species considered in various model cases. The model assumptions are:

Steady state.

Planar symmetry with mass transport in one spatial Cartesian coordinate.

Pressure gradients across layers are negligible.

Isothermal conditions.

All species are in gas phase and are considered an ideal gas mixture.

The catalyst layers are thin enough to be considered as interfaces where the electrochemical reactions take place.

The membrane is assumed to be impermeable enough to neglect diffusion of gases.

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Neglecting diffusion through the membrane simplifies the equations to be solved by decoupling the anode from the cathode. This approximation will not affect the model comparisons but the predictions in the ABL and CBL may not correspond to actual PEMFC operation. With these assumptions one set of mass transport equations model is developed based on the Maxwell–Stefan equations and the other set is developed with the AMC equations. The resulting concentration profiles obtained from these models can be used to compare both approaches.

We used a two component and a three component mixture in the anode: a humidified hydrogen stream (case A-1) and a humidified hydrogen and nitrogen stream (case A-2). The overall electrochemical reaction at the anode catalyst layer (ACL) (i.e., the boundary condition in the model) is represented by

\[ \text{H}_2 \rightarrow 2\text{H}^+ + 2e^- \]  

In the cathode, we also consider a two component and a three component mixture: a humidified oxygen stream (case C-1) and a humidified air stream (case C-2). The overall electrochemical reaction at the cathode catalyst layer (CCL) is represented by

\[ \frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{O} \]  

2.1. Governing equations based on the Maxwell–Stefan model

The Maxwell–Stefan equations for diffusion of an \( \alpha \)-component in an ideal gas mixture through a porous medium in one dimension take the form

\[ \frac{d\rho_\alpha}{dz} = \sum_{\beta=1}^{N} \frac{1}{D_{\alpha\beta}} (y_{\alpha} N_{\beta} - y_{\beta} N_{\alpha}) \]  

where \( y_\alpha \) is the mole fraction of an ideal gas and the molar density for an ideal gas is given by

\[ \rho = \frac{P}{RT} \]  

and the effective diffusion coefficient is given by

\[ D_{\alpha\beta}^{\text{eff}} = \frac{1}{5} D_{\alpha\beta} \]  

In Eq. (5), \( D_{\alpha\beta} \) is the free stream binary diffusion coefficient for species \( \alpha \) and \( \beta \), and \( \delta \) is the porosity of the gas diffusion layer. For convenience a mathematical form equivalent to Eq. (3) is used to solve the species concentration profiles. Thus, Eq. (3) can be rearranged in the form of the Fick’s first law as

\[ N_{\alpha} = y_\alpha \sum_{\beta=1}^{N} N_{\beta} - cD_{\alpha\beta}^{\text{eff}} \frac{d\rho_\alpha}{dz} \]  

where the effective diffusion coefficient of species \( \alpha \) in the mixture is defined as (Treybal, 1980)

\[ D_{\alpha\beta}^{\text{eff}} = \frac{N_{\alpha} - y_\alpha \sum_{\beta=1}^{N} N_{\beta}}{\sum_{\beta=1}^{N} \frac{1}{D_{\alpha\beta}^{\text{eff}}} (y_{\beta} N_{\beta} - y_{\alpha} N_{\alpha})} \]  

The differential mass balance for species \( \alpha \) in the ABL and CBL is

\[ \frac{dN_{\alpha}}{dz} = 0 \]  

which states that the fluxes of the species are constant and independent of position.

2.2. Governing equations based on the AMC model

For the AMC model, diffusion of an \( \alpha \)-component in an ideal gas mixture through a porous medium in one dimension is described by Fick’s first law using Eq. (6). However, the CFD codes may use a mixture diffusion coefficient, see for example Eq. (A4), calculated from binary diffusion coefficients, which is not consistent with the definition required by the Maxwell–Stefan model, Eq. (7). Thus, the AMC definition now requires a correction term in Eq. (6) in order to close the global mass balance. In this work, the AMC equations as used in STAR CD (CD-adapco group, 2004) are tested and Appendix A shows the derivation for the correction term on a molar basis as determined from that methodology. As a result, when Eq. (A4) is used as the definition for \( D_{\alpha\beta} \), Eq. (6) is rewritten as

\[ N_{\alpha} = y_\alpha \left( \sum_{\beta=1}^{N} N_{\beta} \right) - cD_{\alpha\beta}^{\text{eff}} \frac{d\rho_\alpha}{dz} \]  

where the correction term, \( N_c \), is given as

\[ N_c = c \sum_{\alpha=1}^{N} \left( D_{\alpha\beta}^{\text{eff}} \frac{d\rho_\alpha}{dz} \right) \]  

Common CFD techniques use the mass transport equations on a mass fraction basis and additional derivations for the correction term on a molar basis can be found in Martínez (2008). Here however in order to compare this approach with the Maxwell–Stefan equations, the AMC model with a correction term is used on a molar basis.

The same differential mass balance for species \( \alpha \) in the ABL and CBL as given by Eq. (8) is applied for the AMC model and thus the species fluxes are constant and independent of position.

2.3. Boundary conditions

2.3.1. Anode backing layer

At the anode flow channel/ABL interface it is assumed that the concentrations of the species are given by the bulk concentrations in the flow channel. The values for the boundary conditions can be obtained by knowing the relative humidity (RH) of the flow channel stream. Then for case A-1 in the ABL gives

\[ z = 0 : x_{\text{H}_2\text{O}}^A = \frac{P_{\text{sat}}^{\text{H}_2\text{O}}}{P_{\text{H}_2}\rho_{\text{H}_2}} , x_{\text{H}_2}^A = 1 - x_{\text{H}_2\text{O}}^A \]  

where \( P_{\text{sat}}^{\text{H}_2\text{O}} \) is the saturation pressure of water at the temperature of the stream. For case A-2 when a 6:4 ratio of \( \text{H}_2:\text{N}_2 \) on a dry basis
is used, the boundary conditions are

\[ \frac{\partial x_A^A}{\partial z} = \frac{RHA}{p} x_A^A - \frac{d z}{d z} = 0 \quad x_A^A = 0.6 \ (1 - x_A^A), \]

\[ x_A^H = 0.4 \ (1 - x_A^H). \]  

(12)

The jump mass balances (Slattery, 1999) at the ABL/membrane interface requires that for case A-1

\[ N_A^{A,z} x_A^z = -\frac{d z}{d z} x_A^z = 0 \]

\[ N_{x_A}^A = \frac{M_{x_B}}{M_{x_A}}. \]  

(13)

The reaction rate at the interface in Eq. (13) is related to the cell current density:

\[ -\frac{r_{x_A}}{M_{x_A}} = \frac{i}{2F}. \]  

(14)

The molar flux of water through the membrane is only due to electro-osmotic drag since diffusion is neglected as stated in the assumptions. Then the molar flux becomes

\[ \frac{N_{x_A}^M}{z_A} = \frac{\xi_H}{0} i \]  

where \( \xi_H \) is the electro-osmotic drag coefficient of water obtained from Shimpalee (2001). The electro-osmotic drag coefficient is defined as the number of water molecules transported with a hydrogen ion moving in the membrane.

Combining Eq. (8) with Eqs. (13)–(15) give the molar flux for each species throughout the ABL:

\[ \frac{N_{x_A}^A}{z_A} = \frac{2F}{\xi_H} \]  

(16)

For case A-2, in addition to Eq. (16), the jump mass balances (Slattery, 1999) at the ABL/membrane interface requires that

\[ z = z_A : N_{x_A}^A = 0 \]  

(17)

which is also valid throughout the ABL since the fluxes of the species are constant and independent of position.

2.3.2. Cathode backing layer

Similarly to the ABL, at the cathode flow channel/CBL interface it is assumed that the concentrations of the species are given by the bulk concentrations in the flow channel. Then the boundary conditions for case C-1 in the CBL can be written:

\[ z = z_C : x_C^C = -\frac{RHC}{p} x_C^C - \frac{d z}{d z} x_C^C = 0 \]

(18)

For case C-2 (i.e., humid air) in the CBL gives

\[ z = z_C : x_C^C = -\frac{RHC}{p} x_C^C = 0.21 (1 - x_C^C). \]  

(19)

The jump mass balances (Slattery, 1999) at the CBL/membrane interface requires that for case C-1

\[ z = z_C : N_{x_C}^C = \frac{r_{x_C}}{2M_{x_C}} \]

\[ N_{x_C}^C = N_{x_C}^M + \frac{r_{x_C}}{2M_{x_C}}. \]  

(20)

The reaction rates at the interface in Eq. (20) are related to the cell current density:

\[ -\frac{r_{x_C}}{M_{x_C}} = \frac{i}{2F}. \]  

(21)

The molar flux of water through the membrane is given by Eq. (15). Combining Eq. (8) with Eqs. (15), (20) and (21) gives the molar flux for each species throughout the CBL as

\[ N_{x_C}^C = -\frac{i}{4F}. \]  

(22)

For case C-2, in addition to Eq. (22), the jump mass balances (Slattery, 1999) at the CBL/membrane interface requires that

\[ z = z_C : N_{x_C}^C = 0 \]  

(23)

which is also valid throughout the CBL since the fluxes of the species are constant and independent of position.

2.4. Solution to model equations

The general solution to Fick’s first law is

\[ y_A = N_{x_A}^A \frac{N_{x_A}}{N_T^A} + C_{x_A} e^{-N_{x_A} i \frac{d x_A}{d x_{x_A}}}. \]  

(24)

where

\[ N_T = \sum_{x_A} N_{x_A}. \]  

(25)

and \( C_{x_A} \) is the integration constant whose value depends on the boundary condition for the \( \alpha \) component. Eq. (24) is the general analytical solution for the AMC model without the correction factor and it is the equivalent mathematical form of the Maxwell–Stefan equations. The difference depends on the definition of the effective diffusion coefficient used as explained before. In addition, an analytical solution for the Maxwell–Stefan equations of a ternary mixture with one stagnant component is available (Carty & Schrodt, 1975). This solution is equivalent to the solution obtained by combining Eqs. (24) and (7) for cases A-2 and C-2.

For the AMC model with correction term, Eqs. (9) and (10) are combined and the non-linear terms are linearized using the technique from Newman (1991). The differential terms are then approximated by finite difference. In the first iteration concentration profiles are obtained from the numerical solution of the AMC model without the correction term. Subsequent iterations use the solution from the previous iteration to calculate the diffusion coefficient according to Eq. (A4) and new concentration profiles are obtained. Convergence is obtained when the global mass balance is met. This procedure was carried out using the software Maple 9.0.

2.5. Parameters and conditions

The parameters used for the comparisons are shown in Table 1. For the purposes of illustration, the specified current density is below the maximum current density allowed by the model so that the water remains in the vapor phase as assumed and no condensation occurs. That is, the mole fraction of water is below the saturation value of 0.506 for model cases at 101 kPa and below 0.167 for the ternary system.

Estimates for the three gas-pair diffusion coefficients were obtained from the Chapman–Enskog kinetic theory (Bird, Stewart, & Lightfoot, 2002):

\[ D_{\alpha \beta} = C \frac{T^{3/2}}{F}. \]  

(26)

where \( C \) is a function of the critical properties of the \( \alpha \) and \( \beta \) species.

3. Results and discussion

Converged results for the profiles of the individual species are compared in Fig. 2 for the anode side at 101 kPa for the ternary sys-
Table 1
Parameters used in model cases

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( t )</td>
<td>0.7 A/cm² (except otherwise specified)</td>
<td>Specified</td>
</tr>
<tr>
<td>( p_{\text{sat}} )</td>
<td>51.3 kPa (except Fig. 6)</td>
<td>Specified</td>
</tr>
<tr>
<td>( \Delta H_{\text{H}_2} )</td>
<td>114 kPa cm²/s</td>
<td>Bird et al. (2002)</td>
</tr>
<tr>
<td>( \Delta H_{\text{H}_2} )</td>
<td>29.5 kPa cm²/s</td>
<td>Bird et al. (2002)</td>
</tr>
<tr>
<td>( \Delta H_{\text{H}_2} )</td>
<td>30.2 kPa cm²/s</td>
<td>Bird et al. (2002)</td>
</tr>
<tr>
<td>( \Delta H_{\text{N}_2} )</td>
<td>104 kPa cm²/s</td>
<td>Bird et al. (2002)</td>
</tr>
<tr>
<td>( \Delta H_{\text{O}_2} )</td>
<td>28.0 kPa cm²/s</td>
<td>Bird et al. (2002)</td>
</tr>
<tr>
<td>( \Delta H_{\text{N}_2} )</td>
<td>0.5 (except otherwise specified)</td>
<td>Specified</td>
</tr>
<tr>
<td>( T )</td>
<td>355 K (except otherwise specified)</td>
<td>Specified</td>
</tr>
<tr>
<td>( \delta_\text{A} )</td>
<td>0.0356 cm</td>
<td>Bernardi (1990)</td>
</tr>
<tr>
<td>( \delta_\text{C} )</td>
<td>0.4</td>
<td>Bernardi (1990)</td>
</tr>
</tbody>
</table>

Fig. 2. Mole fraction profiles at 101 kPa for case A-2.

Fig. 3. Mole fraction profiles at 101 kPa for case C-2.

Table 2
Difference between Maxwell–Stefan and corrected AMC models predictions for mole fractions at the anode GDL/membrane interface

<table>
<thead>
<tr>
<th>Case</th>
<th>Species</th>
<th>Difference</th>
<th>Mole fraction (Maxwell–Stefan)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-1 (101 kPa)</td>
<td>H₂</td>
<td>0.1%</td>
<td>0.748</td>
</tr>
<tr>
<td>A-1 (101 kPa)</td>
<td>H₂O</td>
<td>0.2%</td>
<td>0.252</td>
</tr>
<tr>
<td>A-1 (304 kPa)</td>
<td>H₂</td>
<td>0.2%</td>
<td>0.920</td>
</tr>
<tr>
<td>A-1 (304 kPa)</td>
<td>H₂O</td>
<td>1.8%</td>
<td>0.080</td>
</tr>
<tr>
<td>A-2 (101 kPa)</td>
<td>H₂</td>
<td>2.0%</td>
<td>0.291</td>
</tr>
<tr>
<td>A-2 (101 kPa)</td>
<td>N₂</td>
<td>2.3%</td>
<td>0.465</td>
</tr>
<tr>
<td>A-2 (101 kPa)</td>
<td>H₂O</td>
<td>2.1%</td>
<td>0.245</td>
</tr>
<tr>
<td>A-2 (304 kPa)</td>
<td>H₂</td>
<td>1.4%</td>
<td>0.359</td>
</tr>
<tr>
<td>A-2 (304 kPa)</td>
<td>N₂</td>
<td>2.5%</td>
<td>0.570</td>
</tr>
<tr>
<td>A-2 (304 kPa)</td>
<td>H₂O</td>
<td>12.9%</td>
<td>0.071</td>
</tr>
</tbody>
</table>

Table 3
Difference between Maxwell–Stefan and corrected AMC models predictions for mole fractions at the membrane/cathode GDL interface

<table>
<thead>
<tr>
<th>Case</th>
<th>Species</th>
<th>Difference</th>
<th>Mole fraction (Maxwell–Stefan)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-1 (101 kPa)</td>
<td>O₂</td>
<td>0.5%</td>
<td>0.689</td>
</tr>
<tr>
<td>C-1 (101 kPa)</td>
<td>H₂O</td>
<td>1.2%</td>
<td>0.311</td>
</tr>
<tr>
<td>C-1 (304 kPa)</td>
<td>O₂</td>
<td>0.3%</td>
<td>0.850</td>
</tr>
<tr>
<td>C-1 (304 kPa)</td>
<td>H₂O</td>
<td>1.4%</td>
<td>0.150</td>
</tr>
<tr>
<td>C-2 (101 kPa)</td>
<td>O₂</td>
<td>1.1%</td>
<td>0.124</td>
</tr>
<tr>
<td>C-2 (101 kPa)</td>
<td>N₂</td>
<td>0.7%</td>
<td>0.564</td>
</tr>
<tr>
<td>C-2 (101 kPa)</td>
<td>H₂O</td>
<td>1.7%</td>
<td>0.312</td>
</tr>
<tr>
<td>C-2 (304 kPa)</td>
<td>O₂</td>
<td>0.2%</td>
<td>0.158</td>
</tr>
<tr>
<td>C-2 (304 kPa)</td>
<td>N₂</td>
<td>0.5%</td>
<td>0.691</td>
</tr>
<tr>
<td>C-2 (304 kPa)</td>
<td>H₂O</td>
<td>2.3%</td>
<td>0.151</td>
</tr>
</tbody>
</table>

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ever, it should be notice that larger differences can be obtained when comparing small numbers. From Table 2 we can obtain that the mole fraction of water at the anode GDL/membrane interface in case A-2 (304 kPa) is $7.10 \times 10^{-2}$ and $7.97 \times 10^{-2}$ for the Maxwell–Stefan and the corrected AMC models, respectively. Although, mathematically this numbers have a difference of more than 5%, it does not represent a significant difference when evaluating the fuel cell. For the PEMFC the direct effect of this difference occurs when calculating properties based on the water content determined by the activity of vapor at the electrode/membrane interface. To evaluate the effect of this difference in a PEMFC, a plot of the membrane conductivity, using the correlation from Springer, Zawodzinski, & Gottesfeld (1991), at 355 K and 304 kPa is shown in Fig. 4 as function of water mole fraction. It can be observed that the mole fraction difference occurs at the lower part of the curve which does not affect significantly the prediction of membrane conductivity. Another property affected by the water mole fraction at the electrode/membrane interface is the diffusion coefficient of water in the membrane. Results presented by Springer et al. (1991) show that the diffusion coefficient of water is in the order of $10^{-6}$ cm$^2$/s at 303 K (i.e., about $1.3 \times 10^{-6}$ cm$^2$/s). Even for the model cases presented in this study at 355 K and 304 kPa the order of magnitude of the diffusion coefficient of water remains the same (i.e., about $4 \times 10^{-6}$ cm$^2$/s). Consequently the diffusion coefficient of water is not affected significantly by a difference in water mole fraction. Similarly, the diffusion coefficient for the other species will not change significantly by such a small difference in the water mole fraction observed in this case.

In order to compare the models the current density was varied for case C-1 at 101 kPa with a relative humidity in the cathode flow channel of 0. For this case, water will start to condensate when the current density reaches a value of about 8.1 A/cm$^2$ and Fig. 5 shows that even at this condition the maximum percent different, which occurs at CCL, is below 5%. Although the maximum percent difference for O$_2$ is increasing, it passes the 5% value in the region after a liquid phase starts to appear and far beyond where the fuel cell operates due to cathode overpotential and membrane resistive losses.

To further compare the models and show the importance of the correction term, a condition corresponding to that typically expected with future high temperature membranes (i.e., 413 K and 304 kPa, and $RH = 0$) was used for case C-1. For this case the largest gradient in oxygen will occur at a maximum current density of 22.4 A/cm$^2$ (i.e., all oxygen reacts at the CCL). This current density is less than the current density for water condensation of 28.5 A/cm$^2$ at these conditions. While these conditions are unrealistic for present-day membranes and PEMFC operation, Fig. 6 provides an idea of how the models compare under extreme conditions. It can be observed that the oxygen profile decreases exponentially from 1.0 to 0 and that at these conditions the correction term increases the accuracy in the species mole fraction relative to that corresponding to the Maxwell–Stefan values, especially for oxygen which have negative values when the $N_e=0$ in Eq. (9). The maximum percent different between the Maxwell–Stefan and the corrected AMC models is 4% for water. For these conditions, the Maxwell–Stefan model predicts an oxygen concentration at the CCL of zero and the AMC model shows a mole fraction of $3.9 \times 10^{-2}$ which is small and not significant.

4. Conclusions

A comparison between the Maxwell–Stefan and the AMC models was presented. Both models provide closure of the overall mass balance with insignificant differences in the species profiles. It was shown that the corrected form of the AMC model shows very reasonable accuracy for calculating the mole fractions of the species in the anode and the cathode as compared to the Maxwell–Stefan model. Although some cases showed a difference larger than 5% for the water, this difference does not affect significantly the prediction of properties which depend on the water mole fraction.

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because the mole fraction is very small. Consequently, the AMC model with the correction term is adequate for PEMFC applications and confusion over solution techniques and mixture diffusion coefficients such as those used by typical CFD providers should not be a topic for discussion of PEMFC predictions. This is especially true when computations of large industrially relevant dimensions are desired and when using the Maxwell–Stefan equations require more computation time and storage capacity due to the coupled nature of that system of equations. In these large 2D and 3D systems these insignificant inaccuracies will be overwhelmed by other assumptions needed to formulate a tractable problem with rapid computations.

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Appendix A. Forms of the correction term on a molar basis

The differential mass balance for species $\alpha$ on a molar basis is written in the following form:

$$\frac{\partial c_{\alpha}}{\partial t} + \nabla \cdot \sum_{\beta=1}^{N} N_{\beta} = \frac{r_{\alpha}}{M_{\alpha}}$$

(A1)

where $r_{\alpha}/M_{\alpha}$ is the reaction term for species $\alpha$.

The molar flux for species $\alpha$ in the mixture can be expressed using Fick’s law by replacing the binary diffusion coefficient with a diffusion coefficient of species $\alpha$ in the mixture:

$$N_{\alpha} = y_{\alpha} \sum_{\beta=1}^{N} N_{\beta} - c_{D_{\alpha m}} \nabla y_{\alpha}$$

(A2)

Combining Eqs. (A1) and (A2) gives the differential mass balance for species $\alpha$ as:

$$\frac{\partial c_{\alpha}}{\partial t} + \nabla \cdot \left[ y_{\alpha} \sum_{\beta=1}^{N} N_{\beta} - c_{D_{\alpha m}} \nabla y_{\alpha} \right] = \frac{r_{\alpha}}{M_{\alpha}}$$

(A3)

In STAR CD $D_{\alpha m}$ is defined using the mole fraction (CD-adapco group, 2004) as

$$D_{\alpha m} = \frac{\sum_{\beta=1}^{N} \beta y_{\beta} M_{\beta}}{M \sum_{\beta=1}^{N} \beta y_{\beta} / D_{\alpha m}}$$

(A4)

Because CFD codes using this definition for $D_{\alpha m}$ are not consistent with the Stefan–Maxwell equations for multi-component combined fluxes, a correction term is defined to ensure global mass conservation. Thus, a correction molar flux, $N_{c}$, is introduced in Eq. (A3). Now, the differential mass balance for species $\alpha$ is written as:

$$\frac{\partial c_{\alpha}}{\partial t} + \nabla \cdot \left[ y_{\alpha} \left( \sum_{\beta=1}^{N} N_{\beta} + N_{c} \right) - c_{D_{\alpha m}} \nabla y_{\alpha} \right] = \frac{r_{\alpha}}{M_{\alpha}}$$

(A5)

The correction molar flux is determined from the overall differential mass balance which is obtained by adding all species equations as follows:

$$\frac{\partial c_{\alpha}}{\partial t} + \nabla \cdot \sum_{\beta=1}^{N} N_{\beta} = -\nabla \cdot \left[ c_{D_{\alpha m}} \nabla y_{\alpha} \right] + \frac{r_{\alpha}}{M_{\alpha}}$$

(A6)

which leads to the correction molar flux as:

$$N_{c} = c \sum_{\alpha=1}^{N} (D_{\alpha m} \nabla y_{\alpha})$$

(A7)

Alternatively, the sum of molar fluxes in Eq. (A3) can be obtained from:

$$\sum_{\beta=1}^{N} N_{\beta} = c \bar{v}$$

(A8)

where $\bar{v}$ is the molar-averaged velocity. Then Eq. (A3) becomes

$$\frac{\partial c_{\alpha}}{\partial t} + \nabla \cdot \left[ c_{\alpha} \bar{v} - c_{D_{\alpha m}} \nabla y_{\alpha} \right] = \frac{r_{\alpha}}{M_{\alpha}}$$

(A9)

In order to ensure global mass conservation a correction molar-averaged velocity, $\bar{v}_{c}$, is introduced in Eq. (A9) so the equation for species $\alpha$ reads:

$$\frac{\partial c_{\alpha}}{\partial t} + \nabla \cdot \left[ c_{\alpha}(\bar{v} + \bar{v}_{c}) - c_{D_{\alpha m}} \nabla y_{\alpha} \right] = \frac{r_{\alpha}}{M_{\alpha}}$$

(A10)

In similar fashion, the correction molar-averaged velocity is determined from the overall differential mass balance which is obtained by adding all species equations as follows:

$$\frac{\partial c_{\alpha}}{\partial t} + \nabla \cdot \left[ \bar{v} c_{\alpha} + c_{\alpha} \bar{v}_{c} - c_{D_{\alpha m}} \nabla y_{\alpha} \right] = \frac{r_{\alpha}}{M_{\alpha}}$$

(A11)

which leads to the correction molar-averaged velocity as:

$$\bar{v}_{c} = \sum_{\alpha=1}^{N} (D_{\alpha m} \nabla y_{\alpha})$$

(A12)

It is clear from Eqs. (A7) and (A12) that

$$N_{c} = c \bar{v}_{c}$$

(A13)

The same correction molar-averaged velocity can also be obtained from a different form of the differential mass balance. Using $\bar{J}_{c}$, the molar flux of species $\alpha$ relative to $\bar{v}$, the differential mass balance for species $\alpha$ can be written in the following form:

$$\frac{\partial c_{\alpha}}{\partial t} + \nabla \cdot \left[ c_{\alpha} \bar{v} + \bar{J}_{c} \right] = \frac{r_{\alpha}}{M_{\alpha}}$$

(A14)

The relative molar flux for species $\alpha$ in the mixture can be expressed using Fick’s law by replacing the binary diffusion coefficient with a diffusion coefficient of species $\alpha$ in the mixture:

$$\bar{J}_{c} = -c_{D_{\alpha m}} \nabla y_{\alpha}$$

(A15)

Combining Eqs. (A14) and (A15) gives the differential mass balance for species $\alpha$ as:

$$\frac{\partial c_{\alpha}}{\partial t} + \nabla \cdot \left[ c_{\alpha} \bar{v} - c_{D_{\alpha m}} \nabla y_{\alpha} \right] = \frac{r_{\alpha}}{M_{\alpha}}$$

(A16)
In order to ensure global mass conservation a correction molar-averaged velocity, $v^*_c$, is introduced in Eq. (A16) so the equation for species $\alpha$ reads:

$$\frac{\partial c}{\partial t} + \nabla \cdot [c(v + v^*_c) - cD_{\text{am}}\nabla y_{\text{g}}] = \frac{r_{\alpha}}{M_{\alpha}}$$  \hspace{1cm} (A17)

The correction molar-averaged velocity is determined from the overall differential mass balance which is obtained by adding all species equations as follows:

$$\frac{\partial c}{\partial t} + \sum_{\alpha=1}^{N} c(v_{\alpha} - c \sum_{\alpha=1}^{N} (D_{\text{am}} \nabla y_{\alpha})) + \sum_{\alpha=1}^{N} \frac{r_{\alpha}}{M_{\alpha}} = \sum_{\alpha=1}^{N} \frac{r_{\alpha}}{M_{\alpha}}$$ \hspace{1cm} (A18)

which leads to the correction molar-averaged velocity as:

$$v^*_c = \sum_{\alpha=1}^{N} (D_{\text{am}} \nabla y_{\alpha})$$ \hspace{1cm} (A19)

References


