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AEROSPACE POWER SCHOLARLY RESEARCH PROGRAM

Delivery Order 0013: Volume 2 - Flux Equations for a Direct Methanol Fuel Cell Solid Polymer Electrolyte Membrane

Sarwan S. Sandhu

University of Dayton
Department of Chemical and Materials Engineering
300 College Park
Dayton, OH 45469-0246

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/s/
JOSEPH P. FELLNER
Senior Chemical Engineer
Fuels Branch
AFRL/PRPA

/s/
BRIAN G. HAGER
Chief
Turbine Engine Division
AFRL/PRPA

/s/
CYNTHIA A. OBRINGER
Deputy Chief
Power Division

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Department of Chemical and Materials Engineering
300 College Park
Dayton, OH 45469-0246

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14. ABSTRACT

This second volume, of a two volume report, consists of the derivation of the transport flux equations for a direct methanol fuel cell solid polymer electrolyte membrane using i) moderately dilute solution theory based on Fickian diffusion, ii) concentrated solution theory based on the generalized Stefan-Maxwell equations, and iii) concentrated solution theory based on the Onsager irreversible thermodynamics approach to transport processes. In very dilute to very concentrated solutions, the developed equations can be used to help determine the transport properties of a membrane such as permeability of the fluid mixture and effective mass diffusivities of the various species.

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Table of Contents

1 Summary

Development of the equations to predict the species (H^+, CH_3OH, H_2O) molar fluxes and ionic current density through the PEM of a DMFC is described. In the Transport Set I section of this report, the equations are based on the extension of moderately dilute solution theory. These equations involve the Fick's law type diffusivities that are strongly dependent on the species concentrations. In the Transport Sets II and III sections of this report, the developments are valid for dilute to very strong solutions. The transport set II is the application of the generalized Maxwell-Stefan equations for the species transport through the PEM. The transport through set III is the result of the application of the Lars Onsager's irreversible thermodynamic approach to transport processes.

2 Introduction

Modeling activity in conjunction with the experimental work is deemed to economically aid in the development of an optimal design of a direct methanol fuel cell (DMFC) for aerospace and ground transportation vehicle applications. To this end, research/ development activity by the principal investigator (P.I.), Sarwan S. Sandhu is given below.

The principal investigator (P.I.) developed a theoretical scheme (see Volume 1 of this report) to predict the reversible cell voltage in the absence of electrode poisoning and methanol crossover through a polymer electrolyte membrane of a DMFC, for example, Nafion® perfluorosulfonic acid polymer and polybenzoxazole or polybenzimidazole based electrolyte membranes. The scheme based on the application of thermodynamic fundamentals of the phase and electrochemical reaction equilibria predicts the reversible voltage at any fuel cell temperature. The effect of nonideal behavior of fluid phases in the anodic and cathodic fluid compartments of a fuel cell on the reversible voltage is accounted for. The simulation is capable of predicting the reversible cell voltage as

function of reactant feed composition and different total pressures in the anode and cathode plenums. The developed reversible voltage equation reduces to the Nernst type equation for the ideal fluid phase behavior of the fuel and oxidant feeds. The predicted reversible cell voltage can be used as an ideal standard to which the actual voltage of a direct methanol fuel cell operating at a given set of reactant feed composition, temperature, and pressure conditions can be compared to evaluate the fuel cell performance.

A senior year undergraduate student, Mr. R. Owen Crowther, typed the entire theoretical development by the P.I. for the reversible cell voltage prediction. The P.I. guided Owen to develop a computer code to simulate the entire set of mathematical equations to generate the reversible cell voltage data as function of temperature, fuel feed composition, and anode and cathode side total pressures.

The actual theoretical development, the computer code, and the code generated numerical data in the form of tables and plots are presented in Report #1 entitled: "Fuel Cell Project: Direct Methanol Fuel Cell: Theoretical Formulation of Reversible, Open-Circuit Voltage for a Direct Methanol Fuel Cell" by Sarwan S. Sandhu, Department of Chemical & Materials Engineering, The University of Dayton, Dayton, Ohio 45469-0246.

Presented in this report volume, the P.I. has developed the mathematical equations to predict the ionic current density and the species (H^+,CH_3OH, H_2O) molar fluxes for their transport through a solid polymer electrolyte or polymer-ceramic material composite membrane of a DMFC at the steady state, isothermal conditions by the application of fundamentals of transport phenomena. The developed transport equations are presented in three sets. In the transport set I, the equations are based on the extension of moderately dilute solution theory. These equations involve the Fick's law type mass diffusivities that are known to be strongly dependent on the species concentrations. The transport equation sets II and III are valid for very strong solutions. The transport equation set II is based on the application of the generalized Maxwell-Stefan equations. The transport equation set III is based on the application of the Lars Onsager's

irreversible thermodynamic approach to transport processes. The developed equations account for the effect of the voltage, pressure and the species concentration gradients on their transport fluxes. These equations, describing species transport fluxes through a solid polymer electrolyte membrane are to be coupled with the equations, yet to be developed, describing mass transfer through the electrode porous backing layers and species mass transport with electrochemical/chemical kinetics in the porous electrode layers. The coupled equations, describing the various phenomena occurring in a DMFC in operation, would be of immense significance in the evaluation of performance and design/development of a DMFC. The usefulness of the developed transport equations may also be seen in that they can be employed to experimentally determine the transport properties of a membrane such as permeability of the fluid mixture and effective mass diffusivities of the species by designing appropriate fuel cell experiments.

The developed transport equations by the P.I. were typed by Mr. Sarath Krishnan, a graduate student in the chemical engineering program at the University of Dayton. Very recently, Mr. R. Owen Crowther (who is now a graduate student in our chemical engineering program) has been guided by the P.I. to simulate the first set of transport equations in the form of a computer code to generate numerical data on current density and species (H^+, CH_3OH, H_2O) molar fluxes through a polymer electrolyte membrane of a DMFC. He is expected to start developing the computer code in the near future.

The actual theoretical development of the transport equations is presented in Report #2 entitled: "Fuel Cell Project: Direct Methanol Fuel Cell: Theoretical Formulation of Transport Fluxes of species (H^+, CH_3OH, H_2O) through a Solid Polymer Electrolyte Membrane (PEM) of a Direct Methanol Fuel Cell," by Sarwan S. Sandhu, Department of Chemical & Materials Engineering, The University of Dayton, Dayton, Ohio 45469-0246.

The P.I. developed a set of equations to predict the reversible as well as irreversible or actual power production from a continuously fed DMFC operating at steady-state conditions. This development is based on the fundamentals of classical thermodynamics

and the species and overall material balances. The scheme requires the information on the reactant feed stream composition, temperature, and pressure conditions at the inlets of a DMFC, fractional conversion of methanol via electrochemical process for the production of electric power, its chemical oxidation at the catalytic surface of the cathode, and the amounts of methanol, water, and hydrogen ions transported through the solid polymer electrolyte membrane from the anode side to the cathode side of a DMFC. The development accounts for the nonideal behavior of the fluid phases. This development is not in the typed form at the time of reporting. Mr. Sarath Krishnan, a graduate student in the chemical engineering program at the University of Dayton has gladly accepted to understand the entire scheme of equations and to present them in the form of a typed report. Also, he would develop a computer code under my direction to generate numerical data on the reversible and actual electric power production as function of input parameter values.

The P.I. studied and carried out partial analysis of the open literature on the research/ development of direct methanol fuel cells depending on availability of time for this equally important activity. Based on the information acquired from the literature on the direct methanol fuel cells and his knowledge of the basic and engineering sciences relevant to the research/development of a DMFC, the P.I. developed an outline of a comprehensive research/development program to develop an efficient DFMC energy conversion system. The outline has been entitled, "Direct Methanol Fuel Cell (DMFC) Research/Development - Theoretical and Experimental Integrated Approach". A copy of this outline was provided to Dr. J.P. Fellner of the Power Division of the WPAFB, Ohio.

The effort by Sarwan S. Sandhu (P.I.), his students and Dr. J. P. Fellner on the research/development activity has resulted in the following presentations and proceedings publications:

"Direct Methanol Polymer Electrolyte Fuel Cell Modeling: Open-Circuit Voltage Equation" in the Proceedings of the 8th International Conference on Electrical and Electronic Products, Vol. 34 (2002), pp. 233-253, Product Safety Corporation,

Sissonville, West Virginia; The Conference held at the Greenbrier, White Sulphur Springs, West Virginia; January 14-16, 2002.

Direct Methanol Polymer Electrolyte Fuel Cell Modeling: Reversible Open Circuit Voltage Equation and Species Flux Equations", presented at the 8th International Symposium on Polymer Electrolytes" held at the Eldorado Hotel, Santa Fe, New Mexico, May 19-24, 2002.

"Direct Methanol Polymer Electrolyte Fuel Cell Modeling," presented at the 2002 AIChE North Central Regional Student Conference. "A Climate Change," Chem-E-Car Competition, University of Michigan, February 7-9, 2002.

3 Methods, Assumptions, and Procedures

Presented in this report volume, the P.I. has developed the mathematical equations to predict the ionic current density and the species (H^+,CH_3OH, H_2O) molar fluxes for their transport through a solid polymer electrolyte or polymer-ceramic material composite membrane of a DMFC at the steady state, isothermal conditions by the application of fundamentals of transport phenomena. The developed transport equations are presented in three sets. In the transport set I section, the equations are based on the extension of moderately dilute solution theory. These equations involve the Fick's law type mass diffusivities that are known to be strongly dependent on the species concentrations. The transport equation sets II and III sections are valid for very strong solutions. The transport equation set II section is based on the application of the generalized Maxwell-Stefan equations. The transport equation set III section is based on the application of the Lars Onsager's irreversible thermodynamic approach to transport processes. The developed equations account for the effect of the voltage, pressure and the species concentration gradients on their transport fluxes. These equations, describing species transport fluxes through a solid polymer electrolyte membrane are to be coupled with the equations, yet to be developed, describing mass transfer through the electrode porous backing layers and species mass transport with electrochemical/chemical kinetics in the porous electrode layers. The coupled equations, describing the various phenomena occurring in a DMFC in operation, would be of immense significance in the evaluation of

performance and design/development of a DMFC. The usefulness of the developed transport equations may also be seen in that they can be employed to experimentally determine the transport properties of a membrane such as permeability of the fluid mixture and effective mass diffusivities of the species by designing appropriate fuel cell experiments.

4 Results and Discussion

4.1 Flux Equations for a Direct Methanol Fuel Cell Solid Polymer Electrolyte Membrane

Derivation of the transport flux equations for a direct methanol fuel cell solid polymer electrolyte membrane using i) moderately dilute solution theory based on Fickian diffusion, ii) concentrated solution theory based on the generalized Stefan-Maxwell equations, and iii) concentrated solution theory based on the Onsager irreversible thermodynamics approach to transport processes are given below.

4.1.1 Transport Set I – Flux Equations using Moderately Dilute Solution Theory

4.1.1.1 Introduction

The transport equations given below are quite general in that they can be applied to any type of membrane (e.g. acid doped polybenzimidazole, *Nafion*® - DuPont, a ceramic (clay: $Al_2O_3.2SiO_2.2H_2O$)- *Nafion*® or PVDF (polyvinylidene floride) composite) with some adjustments if required. The developed equations are presented in the form such that transport and solubility/permeability data either can be obtained from experimental work or available literature. It is assumed here that the geometrical configuration of the membrane is invariant during the isothermal, steady state operation of DMFC.

4.1.1.2 Mathematical Derivation

In general, transport of H^+ through membrane can be considered via diffusion, migration due to electric field and convection dependent upon the pressure difference across the membrane and permeability of the membrane to the fluid mixture of CH_3OH, H_2O, H^+, etc., noting that the membrane permeability is function of its molecular structure and void fraction, $\in$, defined as the ratio of the volume of the interstices between the atoms / functional groups and nanometer /micrometer pores to the total membrane occupied volume.

If the gradient of the H^+ electrochemical potential is used as the driving force for diffusion through membrane in the presence of water or water-methanol mixture, the flux of H^+ per unit area of the membrane perpendicular to the direction of transport of H^+ can be expressed as:

$$\vec{\dot{N}}_{H^+} = \left(\frac{\in u_{H^+}}{\tau} \right) c_{H^+} \left[-\vec{\nabla} \mu_{H^+} \right] + c_{H^+} \vec{v}_o \qquad (1)$$

where u_{H^+} = mobility of H^+ in water or in water-methanol mixture present in the membrane, [$(m^2/s)/(J/mol)$];

τ = tortuosity factor to account for the zigzag path ways for the species transport through the membrane;

$\in$ = void fraction of interstices, nanometer/micrometer size pores acting as pathways for the permeation of H^+, water, and methanol, if methanol crossover is occurring through the membrane;

c_{H^+} = fluid phase concentration of H^+, [mol/m_f^3];

$\mu_{H^+} = \mu_{H^+}^{ch} + z_{H^+} F \Phi$ = electrochemical potential of H^+ in the fluid phase, [J/mol];

$\vec{v}_o$ = superficial fluid phase velocity, [m/s];

$\mu_{H^+}^{ch}$ = chemical potential of H^+ in the fluid phase in the presence of membrane material [J/mol];

z_{H^+} = number of protonic charges on H^+= +1;

F = Faraday's constant, e.g., charge on 1 g-mol of charged H^+ ions = 96487 [coulomb/mol];

Φ = electrical potential,[V].

In the first term on the right hand side of Eq. (1), $\left(\frac{\in u_{H^+}}{\tau}\right)$ is the effective mobility of H^+. This multiplied with $\left(-\vec{\nabla}\mu_{H^+}\right)$ results in the effective velocity for diffusion and migration via electric field, and multiplication by the concentration c_{H^+} results in the contribution to the net flux $\vec{\dot{N}}_{H^+}$. The second term on the right hand side is the contribution to the flux via convective motion of the fluid phase.

The Nernst-Einstein relation is used to express u_{H^+} in terms of D_{H^+} [diffusivity of H^+],

$$u_{H^+} = \frac{D_{H^+}}{RT} \tag{2}$$

where, D_{H^+} = H^+ ion diffusivity in the fluid phase (in water or water-methanol mixture) in the membrane, [m^2/s];

T = temperature, [K];

R = universal gas constant, $\left[8.314 J/mol-K\right]$.

Replacing u_{H^+}, in terms of D_{H^+}, in Eq. (1) leads to

$$\vec{\dot{N}}_{H^+} = \frac{\in D_{H^+}}{\tau}\left(\frac{c_{H^+}}{RT}\right)\left[-\vec{\nabla}\mu_{H^+}\right] + c_{H^+}\vec{v}_o \tag{3}$$

$$\vec{\dot{N}}_{H^+} = D_{H^+,eff}\left(\frac{c_{H^+}}{RT}\right)\left[-\vec{\nabla}\mu_{H^+}\right] + c_{H^+}\vec{v}_o \tag{3a}$$

where $D_{H^+,eff} = \frac{\in D_{H^+}}{\tau}$ = effective diffusivity of H^+ in the fluid phase present in the membrane, [m^2/s].

If the hydrogen ion is chosen to define the electric potential, Φ;

Then, $\mu_{H^+} = \text{RT ln}\left(\frac{c_{H^+}}{c_o}\right) + z_{H^+}\,\text{F}\,\Phi$ (4)

The gradient of the electrochemical potential of any other ionic species i can be written as:

$$\vec{\nabla}\mu_i = \vec{\nabla}\left(\mu_i - \frac{z_i \mu_{H^+}}{z_{H^+}}\right) + \frac{z_i \vec{\nabla}\mu_{H^+}}{z_{H^+}} \qquad (5)$$

Note that in the first term on the right hand side of Eq. (5) the expression within the parentheses is independent of electric potential according to the reference [J.S. Newman, Electrochemical systems, Prentice Hall, 1991].

$$\left(\mu_i - \frac{z_i}{z_{H^+}}\mu_{H^+}\right) = \mathrm{RT}\ln\lambda_i - \frac{z_i}{z_{H^+}}\mathrm{RT}\ln\lambda_{H^+} \qquad (6)$$

where λ_i is the absolute activity of species i; z_i, the number of unitary charges on species i.

$$\lambda_i = a_i^{\theta}\left(\frac{c_i}{c_o}\right) f_i \qquad (6a)$$

where a_i^{θ} = a proportionality constant, independent of composition and electrical state; function of the nature of solute and solvent and dependent on temperature and pressure; for condensed phases the pressure dependence is ignored;

c_i = molar concentration of species i, [mol/liter];

c_o = 1 mol/liter; is introduced here to make a_i^{θ}, [a dimensionless quantity];

f_i = activity coefficient of species, i, to account for non-ideal behavior of species i in the fluid phase present in the membrane, [dimensionless].

Similarly, $\lambda_{H^+} = a_{H^+}^{\theta}\left(\frac{c_{H^+}}{c_o}\right) f_{H^+}$ (6b)

Substituting for λ_i and λ_{H^+} from Eqs. (6a) and (6b) into (6), one obtains:

$$\left(\mu_i - \frac{z_i}{z_{H^+}}\mu_{H^+}\right) = \mathrm{RT}\left[\ln\left(a_i^{\theta}\frac{c_i}{c_o}f_i\right) - \frac{z_i}{z_{H^+}}\ln\left(a_{H^+}^{\theta}\frac{c_{H^+}}{c_o}f_{H^+}\right)\right]$$

$$= \mathrm{RT}\left(\ln a_i^{\theta} - \frac{z_i}{z_{H^+}}\ln a_{H^+}^{\theta}\right) + \mathrm{RT}\left(\ln\frac{c_i}{c_o} - \frac{z_i}{z_{H^+}}\ln\frac{c_{H^+}}{c_o}\right) +$$

$$\mathrm{RT}\left(\ln f_i - \frac{z_i}{z_{H^+}}\ln f_{H^+}\right) \tag{6c}$$

In general for any ionic species, i, the flux equation can be written similar to Eq. (3a).

$$\vec{N}_i = D_{i,eff}\left(\frac{c_i}{RT}\right)\left(-\vec{\nabla}\mu_i\right) + c_i\,\vec{v}_o \tag{7}$$

$\vec{\nabla}\mu_i$ using Eqs. (4), (5), and (6c) is:

$$\vec{\nabla}\mu_i = \vec{\nabla}\left(\begin{array}{l}\mathrm{RT}\left(\ln a_i^{\theta} - \frac{z_i}{z_{H^+}}\ln a_{H^+}^{\theta}\right) + \mathrm{RT}\left(\ln\frac{c_i}{c_o} - \frac{z_i}{z_{H^+}}\ln\frac{c_{H^+}}{c_o}\right) + \\ \mathrm{RT}\left(\ln f_i - \frac{z_i}{z_{H^+}}\ln f_{H^+}\right)\end{array}\right) + \frac{z_i}{z_{H^+}}\vec{\nabla}\mu_{H^+} \tag{7a}$$

$$= \vec{\nabla}\left(\begin{array}{l}\mathrm{RT}\left(\ln a_i^{\theta} - \frac{z_i}{z_{H^+}}\ln a_{H^+}^{\theta}\right) + \mathrm{RT}\left(\ln\frac{c_i}{c_o} - \frac{z_i}{z_{H^+}}\ln\frac{c_{H^+}}{c_o}\right) + \\ \mathrm{RT}\left(\ln f_i - \frac{z_i}{z_{H^+}}\ln f_{H^+}\right)\end{array}\right)$$

$$+\frac{z_i}{z_{H^+}}\vec{\nabla}\left(RT\ln\frac{c_{H^+}}{c_o} + z_{H^+}F\Phi\right)$$

$$\vec{\nabla}\mu_i = \vec{\nabla}\left(\mathrm{RT}\left(\ln a_i^{\theta} - \frac{z_i}{z_{H^+}}\ln a_{H^+}^{\theta}\right)\right) + \vec{\nabla}\left(\mathrm{RT}\ln\frac{c_i}{c_o}\right)$$

$$+\vec{\nabla}\left(RT\left(\ln f_i - \frac{z_i}{z_{H^+}}\ln f_{H^+}\right)\right) + z_i F\,\vec{\nabla}\,\Phi \tag{7b}$$

For the condition of constant temperature, Eq. (7b) becomes

$$\vec{\nabla}\mu_i = \mathrm{RT}\,\vec{\nabla}\ln\left(\frac{c_i}{c_o}\right) + z_i F\,\vec{\nabla}\,\Phi + \mathrm{RT}\vec{\nabla}\left(\ln f_i - \frac{z_i}{z_{H^+}}\ln f_{H^+}\right) \tag{7c}$$

Then, the flux Eq. (7) for the constant temperature, can be written as

$$\vec{N}_i = -\,D_{i,eff}\,\frac{z_i F}{RT}c_i\vec{\nabla}\Phi - D_{i,eff}\,c_i\vec{\nabla}\ln\left(\frac{c_i}{c_o}\right)$$

$$-\,D_{i,eff}\,c_i\vec{\nabla}\left(\ln f_i - \frac{z_i}{z_{H^+}}\ln f_{H^+}\right) + c_i\,\vec{v}_o \tag{8}$$

Simplification of the second term on the right hand side of the Eq. (8) leads to

$$\vec{N}_i = - D_{i,eff} \frac{z_i F}{RT} c_i \vec{\nabla}\Phi - D_{i,eff} \vec{\nabla} c_i$$

$$- D_{i,eff} c_i \vec{\nabla} \left(\ln f_i - \frac{z_i}{z_{H^+}} \ln f_{H^+} \right) + c_i \vec{v}_o \qquad (8a)$$

$$\ln f_i - \frac{z_i}{z_{H^+}} \ln f_{H^+} = \ln f_i - \ln f_{H^+}^{\frac{z_i}{z_{H^+}}} \qquad (8b)$$

$$\ln f_i - \frac{z_i}{z_{H^+}} \ln f_{H^+} = \ln \left(\frac{f_i}{f_{H^+}^{\frac{z_i}{z_{H^+}}}} \right) \qquad (8c)$$

Using the above result in Eq. (8a), the following equation is obtained.

$$\vec{N}_i = - D_{i,eff} \frac{z_i F}{RT} c_i \vec{\nabla}\Phi - D_{i,eff} \vec{\nabla} c_i$$

$$- D_{i,eff} c_i \vec{\nabla} \ln f_{i,H^+} + c_i \vec{v}_o \qquad (8d)$$

where $f_{i,H^+} = \left(\frac{f_i}{f_{H^+}^{\frac{z_i}{z_{H^+}}}} \right)$.

Either from Eqs. (3a) and (4) or from Eq. (8d) directly with i = H^+, one obtains the flux equation for H^+ ions :

$$\vec{N}_{H^+} = - D_{H^+,eff} \frac{z_{H^+} F}{RT} c_{H^+} \vec{\nabla}\Phi - D_{H^+,eff} \vec{\nabla} c_{H^+} + c_{H^+} \vec{v}_o \qquad (9)$$

Note that the activity coefficient f_i of the charged species can be estimated following the procedure given in the literature (Ref. J.S. Newman, Electrochemical systems, pp 86-115, Prentice Hall, 1991 edition).

The superficial velocity $\vec{v}_o$, in Eqs. (8d) and (9), is the volume rate of flow through a unit cross-sectional area of the solid membrane material plus fluid phase, here, composed of water, methanol and H^+. It is averaged over a small region of the membrane facial area

perpendicular to the flow but large with regard to the interstitial micro size pores. The velocity $\vec{v}_o$ can be described by:

$$\vec{v}_o = - \frac{k_{pfM}}{\mu}\left[\vec{\nabla}p - \rho\vec{g} - \rho\left(\frac{\sum_i z_i F\left(-\vec{\nabla}\Phi\right)c_i}{\rho}\right)\right] \tag{10}$$

In this equation, μ is the fluid viscosity [kg/ms]; k_{pfM}, the fluid phase permeability through the membrane, $\left[m^2\right]$. The first term on the right side of Eq. (10) is the pressure gradient related force on the fluid phase, the gravitational force is the second term, and the third term is the net force per unit fluid phase volume due to electric field effect. This term may be labeled as the driving force for the electro-osmotic transport of the fluid phase through the membrane. Also note that c_i is the molar concentration of the ionic species, i (with the charge number z_i) in the fluid phase, with ρ being the fluid phase mass density.

For the transport of the fluid phase perpendicular to the direction of the gravitational field, or, in the situation of the second term on the right hand side of Eq. (10) being negligibly small relative to the first and the third terms; Eq. (10) is reduced to:

$$\vec{v}_o = - \frac{k_{pfM}}{\mu}\left[\vec{\nabla}p - \sum_i z_i F\left(-\vec{\nabla}\Phi\right)c_i\right] \tag{11}$$

In the event, either $\left(-\vec{\nabla}\Phi\right)$ electric field is negligibly small in the membrane space, or there is no electric field in action, then Eq. (11) becomes

$$\vec{v}_o = - \frac{k_{pfM}}{\mu}\left[\vec{\nabla}p\right] \tag{11a}$$

Note that this is the usual Darcy's law for the flow through a porous medium with the pressure gradient as the only driving force for the fluid movement. In the case of the fuel cell, if $\vec{\nabla}p$ is large because of the difference in the total pressures in the anode and the cathode compartments and the small thickness of the membrane, $\vec{v}_o$ may acquire a relatively significant value depending upon the value of k_{pfM} and μ of the fluid phase mixture of water, methanol, and H^+. In the event, $\vec{\nabla}p$ is negligible either due to equal

total pressures in the fuel cell anodic and cathodic compartments or due to a relatively thick membrane, then Eq. (11) becomes:

$$\vec{v}_o = \frac{k_{pfM}}{\mu}\left[\sum_i z_i F\left(-\vec{\nabla}\Phi\right)c_i\right] \tag{11a}$$

$$= \frac{k_{pfM}}{\mu}\left(-\vec{\nabla}\Phi\right)\left[\sum_i z_i F c_i\right] \tag{11b}$$

if it is assumed that the fluid phase is electrically neutral, then,

$$\sum_i z_i F c_i = 0 \tag{11c}$$

Consequently, Eq. (11b) leads to: $\vec{v}_o = \vec{0}$, i.e., there is no effect of the electric field on the fluid convective motion through the membrane. This is not the valid conclusion because the literature does give evidence of the fluid transport through the membrane under the field effect. Then, we have to accept that the membrane material to be charge neutral, but the fluid phase permeating through membrane phase is not charge neutral. The net charge per unit fluid phase volume is ($z_{H^+} c_{H^+} F$). Now, Eq. (11b) is written as:

$$\vec{v}_o = \left(\frac{k_{pfM}}{\mu}\right)\left(-\vec{\nabla}\Phi\right)\left(z_{H^+} c_{H^+} F\right) \tag{11d}$$

Note that $\vec{v}_o$ may have relatively significant value depending on the values of $\left(-\vec{\nabla}\Phi\right)$ [electric field strength in the fluid phase in the membrane], c_{H^+} in the fluid phase in the membrane and k_{pfM}.

For the charge transport by the only H^+ ions in the DMFC; Eq. (11) can be written as

$$\vec{v}_o = -\left(\frac{k_{pfM}}{\mu}\right)\left[\vec{\nabla}p - z_{H^+} F\left(-\vec{\nabla}\Phi\right) c_{H^+}\right] \tag{12}$$

Substituting for $\vec{v}_o$ from Eq. (12) into Eq. (9) and simplification leads to

$$\vec{N}_{H^+} = \left[\left(\frac{z_{H^+} F}{RT}\right) D_{H^+,eff} c_{H^+} + \left(\frac{k_{pfM}}{\mu}\right) z_{H^+} F c_{H^+}^2\right]\left(-\vec{\nabla}\Phi\right) + D_{H^+,eff}\left(-\vec{\nabla} c_{H^+}\right) + \left(\frac{k_{pfM}}{\mu}\right) c_{H^+}\left(-\vec{\nabla}p\right) \tag{13}$$

Note the structure of the individual terms contributing to the flux of H^+ ion through the membrane. In the first term on the right hand side of the Eq. (13), $\left(-\vec{\nabla}\Phi\right)$, the electric field is acting as the driving force and $\left(-\vec{\nabla}c_{H^+}\right)$ and $\left(-\vec{\nabla}p\right)$ are the concentration and pressure gradient driving forces in the second and third terms, respectively.

Substitute for $\vec{v}_o$ from Eq. (12) into Eq. (8d) to obtain:

$$\vec{\dot{N}}_i = \left[\left(\frac{z_i F}{RT}\right)D_{i,eff}c_i + \left(\frac{k_{pfM}}{\mu}\right)z_{H^+}Fc_{H^+}c_i\right]\left(-\vec{\nabla}\Phi\right) + D_{i,eff}\left(-\vec{\nabla}c_i\right) +$$

$$D_{i,eff}\ c_i\left(-\vec{\nabla}\ln f_{i,H^+}\right) + \left(\frac{k_{pfM}}{\mu}\right)c_i\left(-\vec{\nabla}p\right) \qquad (14)$$

where $f_{i,H^+} = \left(\frac{f_i}{f_{H^+}^{\frac{z_i}{z_{H^+}}}}\right)$. (14a)

This equation is valid for any ionic and non-ionic species.

Methanol and water are charge neutral species, i.e., $z_{CH_3OH} = z_{H_2O} = 0$, i.e., number of charges on each of these species is zero.

Also, $f_{i,H^+} = \left(\frac{f_i}{f_{H^+}^{o}}\right) = f_i$ (activity coefficients of the charged neutral species i)

Equation (14) is written for a charge neutral species i as:

$$\vec{\dot{N}}_i = \left(\frac{k_{pfM}}{\mu}\right)z_{H^+}Fc_{H^+}c_i\left(-\vec{\nabla}\Phi\right) + D_{i,eff}\left(-\vec{\nabla}c_i\right) +$$

$$D_{i,eff}\ c_i\left(-\vec{\nabla}\ln f_i\right) + \left(\frac{k_{pfM}}{\mu}\right)c_i\left(-\vec{\nabla}p\right) \qquad (15)$$

For the situation where it is reasonable to assume that $\left(\vec{\nabla}\ln f_i\right) = 0$, i.e., variation of f_i across the membrane is negligible; Eq. (15) becomes:

$$\vec{\dot{N}}_i = \left(\frac{k_{pfM}}{\mu}\right)z_{H^+}Fc_{H^+}c_i\left(-\vec{\nabla}\Phi\right) + D_{i,eff}\left(-\vec{\nabla}c_i\right) + \left(\frac{k_{pfM}}{\mu}\right)c_i\left(-\vec{\nabla}p\right) \qquad (16)$$

where, i = CH_3OH, H_2O.

Note that the first term on the right hand side of Eq. (16) involves $\left(-\vec{\nabla}\Phi\right)$, electric field as the driving force even for a charge neutral species such as CH_3OH, H_2O, for example. Here this term is labeled as the electro-osmotic contribution to the flux of charge neutral species i through the membrane. The second term on the right side is the diffusion contribution to the flux of species i and the third term accounts for the flux contribution by the fluid motion set up by $\left(-\vec{\nabla}p\right)$, the pressure gradient in the case of different total pressures in the anode and cathode compartments. Note that the electro-osmotic flux contribution does depend on the fluid phase viscosity, μ, its permeability through membrane, k_{pfM}, and H^+ ion molar concentration in the fluid phase in the membrane matrix.

4.1.1.3 One-Dimensional, Steady-State, and Isothermal

We shall now concentrate on obtaining the equations for the transport of species H^+, CH_3OH, and H_2O through the membrane under the steady state, isothermal conditions for the one-dimensional (x-) case.

The x-components of Eqs. (13) and (16) are:

$$\dot{N}_{H^+,x} = \left[\left(\frac{z_{H^+}F}{RT}\right)D_{H^+,eff}\,c_{H^+} + \left(\frac{k_{pfM}}{\mu}\right)z_{H^+}Fc_{H^+}^2\right]\left(-\frac{\partial\Phi}{\partial x}\right) + D_{H^+,eff}\left(-\frac{\partial c_{H^+}}{\partial x}\right) + \left(\frac{k_{pfM}}{\mu}\right)c_{H^+}\left(-\frac{\partial p}{\partial x}\right) \quad (17a)$$

$$\dot{N}_{i,x} = \left(\frac{k_{pfM}}{\mu}\right)z_{H^+}Fc_{H^+}c_i\left(-\frac{\partial\Phi}{\partial x}\right) + D_{i,eff}\left(-\frac{\partial c_i}{\partial x}\right) + \left(\frac{k_{pfM}}{\mu}\right)c_i\left(-\frac{\partial p}{\partial x}\right) \quad (17b)$$

(molar flux for a charge neutral species, i = CH_3OH, H_2O)

The current density per unit area, perpendicular to x-coordinate in the membrane, is given by:

$$j_x = \sum_{i=1}^{i=3}\left[(z_i F)\dot{N}_{i,x}\right] \tag{18}$$

$$= z_{H^+}\,\mathrm{F}\,\dot{N}_{H^+,x} + z_{CH_3OH}F\dot{N}_{CH_3OH,x} + z_{H_2O}F\dot{N}_{H_2O,x} \tag{18a}$$

$$= z_{H^+}\,\mathrm{F}\,\dot{N}_{H^+,x} \tag{18b}$$

Note that the H^+ ion is the only charge carrier through the membrane so that the transference number of the species H^+ is one.

Using Eq. (17a) for $\dot{N}_{H^+,x}$ in Eq. (18b),

$$j_x = \left[\left(\frac{z_{H^+}^2F^2}{RT}\right)D_{H^+,eff}c_{H^+} + \left(\frac{k_{pfM}}{\mu}\right)z_{H^+}^2F^2c_{H^+}^2\right]\left(-\frac{\partial\Phi}{\partial x}\right) + z_{H^+}\,\mathrm{F}\,D_{H^+,eff}\left(-\frac{\partial c_{H^+}}{\partial x}\right) + \left(\frac{k_{pfM}}{\mu}\right)c_{H^+}\,z_{H^+}\,\mathrm{F}\left(-\frac{\partial p}{\partial x}\right) \tag{19}$$

$$= \left[\left(\frac{z_{H^+}^2F^2}{RT}\right)D_{H^+,eff}c_{H^+}\right]\left(-\frac{\partial\Phi}{\partial x}\right) + \left(\frac{k_{pfM}}{\mu}\right)z_{H^+}^2F^2c_{H^+}^2\left(-\frac{\partial\Phi}{\partial x}\right) + z_{H^+}\,\mathrm{F}\,D_{H^+,eff}\left(-\frac{\partial c_{H^+}}{\partial x}\right) + \left(\frac{k_{pfM}}{\mu}\right)c_{H^+}\,z_{H^+}\,\mathrm{F}\left(-\frac{\partial p}{\partial x}\right) \tag{20}$$

Equation (20) requires the explanation to various terms. The first term on the right hand side expresses transport via H^+ ion movement due to the action of the electric field in the x-direction. The coefficient of $\left(-\frac{\partial\Phi}{\partial x}\right)$ is here defined as the electric conductance of H^+ through fluid phase present in the membrane matrix, i.e.,

$$\kappa_{elec} = z_{H^+}^2F^2\left(\frac{D_{H^+,eff}}{RT}\right)c_{H^+} = z_{H^+}^2F^2\,u_{H^+}\,c_{H^+} \tag{20a}$$

where $u_{H^+}\left[\begin{array}{l}\textit{ion mobility in the fluid composed of}\\ \left(CH_3OH, H_2O, \textit{and } H^+\right)\textit{present in the membrane}\end{array}\right] = \left(\frac{D_{H^+,eff}}{RT}\right)$ (20b)

The second term on the right-hand side of the Eq. (20) explains the current density contribution associated with the fluid "bulk motion" created by the action of electric field on H^+ ions present in the fluid. Third term is the current density contribution because of

gradient in the H^+ ion concentration. Fourth term is the contribution to the current density if the pressure gradient prevails for the different total pressures across the membrane in the electrode chambers.

Equation (20) may now be written as

$$j_x = \kappa_{elec}\left(-\frac{d\Phi}{\partial x}\right)+\left(\frac{k_{pfM}}{\mu}\right)\left(z_{H^+}Fc_{H^+}\right)^2\left(-\frac{d\Phi}{\partial x}\right)+$$

$$z_{H^+}FD_{H^+,eff}\left(-\frac{dc_{H^+}}{dx}\right)+\left(\frac{k_{pfM}}{\mu}\right)\left(z_{H^+}Fc_{H^+}\right)\left(-\frac{dp}{\partial x}\right) \qquad (21)$$

For the medium of assumed uniform dielectric constant (here that of water or of water-methanol mixture present in the membrane), the Poisson equation is used to relate the Laplacian of the electric potential to the charge density in the fluid phase in the membrane:

$$\vec{\nabla}^2\Phi = -\frac{F}{\in}\sum_i z_i c_i \qquad (22)$$

$$= -\frac{F}{\in}\left[z_{H^+}c_{H^+}\right], \qquad (22a)$$

where $\in$ = permittivity of the medium (here that of the fluid phase)

= (dielectric constant) ($\in_0$, permittivity of the free space)

$$= (\text{dielectric constant})\left(8.8542*10^{-14}\,\frac{coulomb}{volt-cm}\right)$$

$$= (\text{dielectric constant of the fluid phase})\left(8.8542*10^{-12}\,\frac{coulomb}{volt-m}\right)$$

$$F = \text{Faraday's constant} = 96487\,\frac{\text{coulomb}}{\text{mole of unitary charges}}$$

For the one-dimensional (x-) case, Eq. (22a) becomes:

$$\frac{d^2\Phi}{dx^2} = -\frac{F}{\in}\left[z_{H^+}c_{H^+}\right] \qquad (22b)$$

The material balance or continuity equation for a component i for the steady state condition, with no reaction, is:

$$\vec{\nabla} \bullet \vec{\dot{N}}_i = 0 \tag{23}$$

$$\frac{d\dot{N}_{i,x}}{dx} + \frac{d\dot{N}_{i,y}}{dy} + \frac{d\dot{N}_{i,z}}{dz} = 0 \tag{23a}$$

For the one-dimensional component in the x-direction,

$$\frac{dN_{i,x}}{dx} = 0 \tag{23b}$$

Using Eq. (17a), the following equation is obtained from Eq. (23b) under the assumption of constant $\left(\frac{d\Phi}{dx}\right)$, $\left(\frac{dp}{dx}\right)$, k_{pfM}, μ and $D_{H^+,eff}$ for the isothermal cell operation.

$$\left[\left(\frac{z_{H^+}F}{RT}\right)D_{H^+,eff}\frac{dc_{H^+}}{dx} + \left(\frac{k_{pfM}}{\mu}\right)z_{H^+}F\,2c_{H^+}\frac{dc_{H^+}}{dx}\right]\left(-\frac{d\Phi}{dx}\right) + D_{H^+,eff}\left(-\frac{d^2c_{H^+}}{dx^2}\right)$$

$$+\left(\frac{k_{pfM}}{\mu}\right)\frac{dc_{H^+}}{dx}\left(-\frac{dp}{dx}\right) = 0 \tag{23c}$$

The modified continuity equation for the fluid mixture of (H_2O, CH_3OH, and H^+) through the nano/micro porous medium is applied for the permeation of fluid phase mixture through the electrolyte membrane at the steady state conditions.

$$\vec{\nabla} \bullet \left[\rho \vec{v}_o\right] = 0, \tag{24}$$

where ρ = fluid-phase density.

For the one-dimensional (x-component) case, Eq. (24) is written as:

$$\frac{d}{dx}\left(\rho v_{o,x}\right) = 0 \tag{24a}$$

The solution of Eq. (24a) is

$$\left(\rho v_{o,x}\right)_{@\,x=0} = \left(\rho v_{o,x}\right)_{@\,x=\delta_M} = \dot{m}_o = \text{constant}, \tag{24b}$$

where $\dot{m}_o$ = superficial fluid mass flux permeating through the membrane along x-axis per unit time per unit area of the membrane perpendicular to the x-axis.

The x-component of Eq. (12) is

$$v_{o,x} = \left(\frac{k_{pfM}}{\mu}\right)\left[\left(-\frac{dp}{dx}\right) + z_{H^+}Fc_{H^+}\left(-\frac{d\Phi}{dx}\right)\right] \tag{24c}$$

The fluid phase mass flux is related to the pressure and electrical gradients as follows:

$$\dot{m}_o = \rho \; v_{o,x} = \left(\frac{\rho k_{pfM}}{\mu} \right) \left[\left(-\frac{dp}{dx} \right) + z_{H^+} F c_{H^+} \left(-\frac{d\Phi}{dx} \right) \right] \tag{24d}$$

For the electric potential distribution, Eq. (22b) is written as

$$\frac{d^2\Phi}{dx^2} = -\frac{F}{\in} \left[z_{H^+} \bar{c}_{H^+} \right], \tag{25}$$

where $\bar{c}_{H^+}$ is the H^+ ion average concentration defined as

$$\bar{c}_{H^+} = \frac{\int_{x=0}^{x=\delta_M} c_{H^+} \, dx}{\delta_M}, \tag{25a}$$

where δ_M = thickness of the membrane. In fact, one may approximate this quite reasonably by

$$\bar{c}_{H^+} = \frac{c_{H^+}^A + c_{H^+}^C}{2} \tag{26}$$

where $c_{H^+}^A$ is the H^+ ion concentration in the fluid phase at the anode-membrane interface and $c_{H^+}^C$ the concentration of H^+ at the membrane-cathode interface on the membrane side. For the situation of relatively fast electrode kinetics associated with the electrochemical reactions, especially fast kinetics at the cathode, the H^+ ion concentration at the membrane-cathode interface, $c_{H^+}^C$ may be approximately set equal to zero. Thus,

$$\bar{c}_{H^+} \cong \frac{c_{H^+}^A}{2} \tag{26a}$$

Equation (25) is solved using the following boundary conditions:

At x = 0, $\Phi = \Phi^A$ (electric potential in the fluid phase at the anode-membrane interface) (27a)

At x = δ_M, $\Phi = \Phi^C$ (electric potential in the fluid phase at the cathode-membrane interface) (27b)

The solution to Eq. (25) is

$$(\Phi - \Phi^A) = (\Phi^C - \Phi^A) \left(\frac{x}{\delta_M} \right) + \left(\frac{z_{H^+} \bar{c}_{H^+} F}{2 \in} \right) \left(\delta_M x - x^2 \right) \tag{28}$$

Note: Here, $(\Phi^C - \Phi^A)$ = -(absolute value of the cell voltage)

$$= -\left|\Phi^C - \Phi^A\right|$$

Note that Eq. (28) describes the electric potential in the fluid present in the interstices in the membrane matrix.

From Eq. (28) one obtains

$$\frac{d\Phi}{dx} = \left(\frac{\Phi^C - \Phi^A}{\delta_M}\right) + \left(\frac{z_{H^+}\bar{c}_{H^+}F}{2 \in}\right)\left(\delta_M - 2x\right) \tag{29}$$

$$= -\frac{\left|\Phi^C - \Phi^A\right|}{\delta_M} + \left(\frac{z_{H^+}\bar{c}_{H^+}F}{2 \in}\right)\left(\delta_M - 2x\right) \tag{29a}$$

The result in Eq. (29) is used in Eq. (24d) and the resultant equation is solved for the pressure distribution in the fluid phase in the membrane matrix to obtain

$$\left(p - p^{t,A}\right) =$$

$$-\left(\frac{\dot{m}_o \mu \delta_M}{k_{pfM}\bar{\rho}}\right)\left(\frac{x}{\delta_M}\right) - z_{H^+}\bar{c}_{H^+}F\left[\left(\Phi^C - \Phi^A\right)\left(\frac{x}{\delta_M}\right) + \left(\frac{z_{H^+}\bar{c}_{H^+}F\delta_M^2}{2 \in}\right)\left(\frac{x}{\delta_M} - \left(\frac{x}{\delta_M}\right)^2\right)\right], \tag{30}$$

where $(\Phi^C - \Phi^A)$ = -(absolute value of the cell voltage),

$p^{t,A}$ = total pressure at the anode-membrane interface,

$\bar{\rho}$ = average fluid density = $\frac{\rho^A + \rho^C}{2}$, where ρ^A and ρ^C are the fluid densities at the anode-membrane and cathode-membrane interfaces, respectively.

Using the boundary condition of $p = p^{t,C}$ (total pressure at the membrane-cathode interface) at $x = \delta_M$, one obtains the following result from Eq. (30):

$$\dot{m}_o = \left(\frac{k_{pfM}\bar{\rho}}{\mu}\right)\left[\frac{p^{t,A} - p^{t,C}}{\delta_M} + z_{H^+}\bar{c}_{H^+}F\frac{\left|\Phi^C - \Phi^A\right|}{\delta_M}\right] \tag{31}$$

This equation shows the effect of the pressure and electric potential differences on the permeation flux of the fluid phase through the membrane. For the case of $p^{t,A}$ (total pressure at the anode) greater than $p^{t,C}$ (total pressure at the cathode), both of these

driving forces are seen to cause the fluid phase to move towards the cathode. For the case $p^{t,A} < p^{t,C}$, the effect of these driving forces on $\dot{m}_o$ is opposite. For the case of $p^{t,A} = p^{t,C}$, Eq. (31) becomes:

$$\dot{m}_o = \left(\frac{k_{pfM}\,\bar{\rho}}{\mu\,\delta_M}\right)\left(z_{H^+}\,\bar{c}_{H^+}\,F\left(\left|\Phi^C - \Phi^A\right|\right)\right) \tag{32}$$

This simple result tells us that due to the electric field effect there is a flux of fluid mixture that permeates through the membrane. For a membrane of given molecular configuration, one way to decrease $\dot{m}_o$; therefore, to decrease the flux of methanol is to increase the membrane thickness. Other way is to use a membrane of such a molecular structure/configuration that the permeability, k_{pfM}, is decreased in such a way that permeation of methanol is selectively reduced more than water with either no or enhancement effect on the permeation of H^+ ions.

Using Eq. (15), one-dimensional molar fluxes of H_2O and CH_3OH through the membrane are

$$\dot{N}_{CH_3OH,x} = \left(\frac{k_{pfM}}{\mu}\right) c_{CH_3OH}\,(z_{H^+}\,F c_{H^+})\left(-\frac{d\Phi}{dx}\right) + D_{CH_3OH,eff}\left(-\frac{dc_{CH_3OH}}{dx}\right) +$$

(electro-osmotic transport) (diffusion transport)

$$+\left(\frac{k_{pfM}}{\mu}\right) c_{CH_3OH}\left(-\frac{dp}{dx}\right) \tag{33}$$

(pressure gradient transport)

$$\dot{N}_{H_2O,x} = \left(\frac{k_{pfM}}{\mu}\right) c_{H_2O}\,(z_{H^+}\,F c_{H^+})\left(-\frac{d\Phi}{dx}\right) + D_{H_2O,eff}\left(-\frac{dc_{H_2O}}{dx}\right) +$$

(electro-osmotic transport) (diffusion transport)

$$+\left(\frac{k_{pfM}}{\mu}\right) c_{H_2O}\left(-\frac{dp}{dx}\right) \tag{34}$$

(pressure gradient transport)

For the condition of the steady state, the local continuity equations for H_2O and CH_3OH are

$$\left(\frac{d\dot{N}_{CH_3OH,x}}{dx}\right) = 0 \qquad (35a)$$

$$\left(\frac{d\dot{N}_{H_2O,x}}{dx}\right) = 0 \qquad (35b)$$

Substitution for $\dot{N}_{CH_3OH,x}$ and $\dot{N}_{H_2O,x}$ from Eqs. (33) and (34) into Eqs. (35a) and (35b), respectively, and simplification leads to

$$\left(\frac{k_{pfM}}{\mu}\right)\frac{d}{dx}\left[c_{CH_3OH}(z_{H^+}Fc_{H^+})\left(-\frac{d\Phi}{dx}\right)\right] + D_{CH_3OH,eff}\left(-\frac{d^2c_{CH_3OH}}{dx^2}\right) +$$

$$+\left(\frac{k_{pfM}}{\mu}\right)\frac{d}{dx}\left[c_{CH_3OH}\left(-\frac{dp}{dx}\right)\right] = 0 \qquad (36a)$$

$$\left(\frac{k_{pfM}}{\mu}\right)\frac{d}{dx}\left[c_{H_2O}(z_{H^+}Fc_{H^+})\left(-\frac{d\Phi}{dx}\right)\right] + D_{H_2O,eff}\left(-\frac{d^2c_{H_2O}}{dx^2}\right) +$$

$$+\left(\frac{k_{pfM}}{\mu}\right)\frac{d}{dx}\left[c_{H_2O}\left(-\frac{dp}{dx}\right)\right] = 0 \qquad (36b)$$

From the Eq. (24d), with the assumption of constant $\left(\frac{k_{pfM}}{\mu}\right)$ and constant fluid phase density ρ in the membrane phase, the following equations are obtained:

$$\left(\frac{k_{pfM}}{\mu}\right)\frac{d}{dx}\left[c_{CH_3OH}(z_{H^+}Fc_{H^+})\left(-\frac{d\Phi}{dx}\right)\right] =$$

$$\left(\frac{\dot{m}_o}{\rho}\right)\frac{dc_{CH_3OH}}{dx}-\left(\frac{k_{pfM}}{\mu}\right)\frac{d}{dx}\left[c_{CH_3OH}\left(-\frac{dp}{dx}\right)\right] \qquad (37a)$$

$$\left(\frac{k_{pfM}}{\mu}\right)\frac{d}{dx}\left[c_{H_2O}(z_{H^+}Fc_{H^+})\left(-\frac{d\Phi}{dx}\right)\right] =$$

$$\left(\frac{\dot{m}_o}{\rho}\right)\frac{dc_{H_2O}}{dx}-\left(\frac{k_{pfM}}{\mu}\right)\frac{d}{dx}\left[c_{H_2O}\left(-\frac{dp}{dx}\right)\right] \qquad (37b)$$

Substitutions are made from Eqs. (37a) and (37b) for $\left(\frac{k_{pfM}}{\mu}\right)\frac{d}{dx}\left[c_{CH_3OH}(z_{H^+}Fc_{H^+})\left(-\frac{d\Phi}{dx}\right)\right]$ and $\left(\frac{k_{pfM}}{\mu}\right)\frac{d}{dx}\left[c_{H_2O}(z_{H^+}Fc_{H^+})\left(-\frac{d\Phi}{dx}\right)\right]$ into Eqs.(36a) and (36b), respectively, to obtain, after simplification, the following results:

$$\frac{d^2c_{CH_3OH}}{dx^2}-\left(\frac{\dot{m}_o}{\rho D_{CH_3OH,eff}}\right)\frac{dc_{CH_3OH}}{dx} = 0 \qquad (38a)$$

$$\frac{d^2c_{H_2O}}{dx^2}-\left(\frac{\dot{m}_o}{\rho D_{H_2O,eff}}\right)\frac{dc_{H_2O}}{dx} = 0 \qquad (38b)$$

These ordinary differential equations are solved using the following boundary conditions:

At x = 0 (membrane-anode interface);

$$c_{CH_3OH} = c^M_{CH_3OH,x=0}, \qquad c_{H_2O} = c^M_{H_2O,x=0} \qquad (39a,b)$$

At x = δ_M (membrane-cathode interface);

$$c_{CH_3OH} = c^M_{CH_3OH,x=\delta_M}, \qquad c_{H_2O} = c^M_{H_2O,x=\delta_M} \tag{40a,b}$$

The solution of the differential Eqs. (38a) and (38b) based on the boundary conditions Eqs. (39) and (40), is

$$c_{CH_3OH} = c^M_{CH_3OH,x=\delta_M} + (c^M_{CH_3OH,x=0} - c^M_{CH_3OH,x=\delta_M})\left(\frac{e^{\alpha_1 x} - e^{\alpha_1 \delta_M}}{1 - e^{\alpha_1 \delta_M}}\right), \tag{41}$$

where $\alpha_1 = \dfrac{\dot{m}_o}{\rho D_{CH_3OH,eff}}$. (41a)

$$c_{H_2O} = c^M_{H_2O,x=\delta_M} + (c^M_{H_2O,x=0} - c^M_{H_2O,x=\delta_M})\left(\frac{e^{\alpha_2 x} - e^{\alpha_2 \delta_M}}{1 - e^{\alpha_2 \delta_M}}\right) \tag{42}$$

where $\alpha_2 = \dfrac{\dot{m}_o}{\rho D_{H_2O,eff}}$. (42a)

Methanol and water concentrations in the membrane matrix at the interfaces with the porous electrodes are now related to their concentrations in the fluid mixtures in the electrodes using the phase equilibrium condition.

At the membrane-anode interface, x = 0;

$$a^M_{CH_3OH,x=0} = a^A_{CH_3OH,x=0}, \tag{43a}$$

$$a^M_{H_2O,x=0} = a^A_{H_2O,x=0}, \tag{43b}$$

where a_i = activity of species i.

Expressing the activities in terms of molar concentrations,

$$\left[\frac{c^{M}_{CH_3OH,x=0}\, f^{M}_{CH_3OH}}{c_o}\right] = \left[\frac{c^{A}_{CH_3OH,x=0}\, f^{A}_{CH_3OH}}{c_o}\right] \tag{44a}$$

$$\left[\frac{c^{M}_{H_2O,x=0}\, f^{M}_{H_2O}}{c_o}\right] = \left[\frac{c^{A}_{H_2O,x=0}\, f^{A}_{H_2O}}{c_o}\right] \tag{44b}$$

where c_i = molar concentration of a species,

$f_i^{\,M}$ = activity coefficient of species i in the fluid phase in the membrane phase,

$f_i^{\,A}$ = activity coefficient of species i in the fluid phase in the porous anode,

c_o = normalization concentration = 1 (mol/liter).

Equations (44a) and (44b) leads to

$$c^{M}_{CH_3OH,x=0} = c^{A}_{CH_3OH,x=0}\left(\frac{f^{A}_{CH_3OH}}{f^{M}_{CH_3OH}}\right) \tag{45a}$$

$$c^{M}_{H_2O,x=0} = c^{A}_{H_2O,x=0}\left(\frac{f^{A}_{H_2O}}{f^{M}_{H_2O}}\right) \tag{45b}$$

Similarly, at the membrane-cathode interface at x = δ_M ,

$$c^{M}_{CH_3OH,x=\delta_M} = c^{C}_{CH_3OH,x=\delta_M}\left(\frac{f^{C}_{CH_3OH}}{f^{M}_{CH_3OH}}\right) \tag{46a}$$

$$c^{M}_{H_2O,x=\delta_M} = c^{C}_{H_2O,x=\delta_M}\left(\frac{f^{C}_{H_2O}}{f^{M}_{H_2O}}\right) \tag{46b}$$

At first approximation; particularly, for the situation of non-availability of the $f_i^{\,M}$ data in the membrane phase, one may take:

$$\left(\frac{f_i^{\,A}}{f_i^{\,M}}\right) \cong 1, \text{ and } \left(\frac{f_i^{\,C}}{f_i^{\,M}}\right) \cong 1.$$

From Eq. (24d),

$$\left[z_{H^+} F c_{H^+}\left(-\frac{d\Phi}{dx}\right)\right] = \dot{m}_o\left(\frac{\mu}{k_{pfM}\,\rho}\right) - \left(-\frac{dp}{dx}\right) \tag{47}$$

On substitution for $\left[z_{H^+} F c_{H^+}\left(-\frac{d\Phi}{dx}\right)\right]$ from Eq. (47) into Eqs. (33) and (34) to obtain, after simplification,

$$\dot{N}^{M}_{CH_3OH,x} = \left(\frac{\dot{m}_o}{\rho}\right) c_{CH_3OH} + D_{CH_3OH,eff}\left(-\frac{dc_{CH_3OH}}{dx}\right) \tag{48a}$$

$$\dot{N}^{M}_{H_2O,x} = \left(\frac{\dot{m}_o}{\rho}\right) c_{H_2O} + D_{H_2O,eff}\left(-\frac{dc_{H_2O}}{dx}\right) \tag{48b}$$

From Eqs. (41) and (42),

$$\left(\frac{dc_{CH_3OH}}{dx}\right) = \left(c^{M}_{CH_3OH,x=0} - c^{M}_{CH_3OH,x=\delta_M}\right)\left(\frac{\alpha_1}{1-e^{\alpha_1\delta_M}}\right)e^{\alpha_1 x} \tag{49a}$$

$$\left(\frac{dc_{H_2O}}{dx}\right) = \left(c^{M}_{H_2O,x=0} - c^{M}_{H_2O,x=\delta_M}\right)\left(\frac{\alpha_2}{1-e^{\alpha_2\delta_M}}\right)e^{\alpha_2 x} \tag{49b}$$

On substitution for $\left(\frac{dc_{CH_3OH}}{dx}\right)$ and $\left(\frac{dc_{H_2O}}{dx}\right)$ from Eqs. (49a) and (49b) into Eqs. (48a) and (48b), respectively, the following expressions are obtained for methanol and water fluxes:

$$\dot{N}^{M}_{CH_3OH,x} = \left(\frac{\dot{m}_o}{\rho}\right)\left(c^{M}_{CH_3OH,x=\delta_M} - \left(c^{M}_{CH_3OH,x=0} - c^{M}_{CH_3OH,x=\delta_M}\right)\left(\frac{e^{\alpha_1\delta_M}}{1-e^{\alpha_1\delta_M}}\right)\right) \tag{50}$$

$$\text{where } \alpha_1 = \frac{\dot{m}_o}{\rho D_{CH_3OH,eff}}. \tag{50a}$$

$$\dot{N}^{M}_{H_2O,x} = \left(\frac{\dot{m}_o}{\rho}\right)\left(c^{M}_{H_2O,x=\delta_M} - \left(c^{M}_{H_2O,x=0} - c^{M}_{H_2O,x=\delta_M}\right)\left(\frac{e^{\alpha_2\delta_M}}{1-e^{\alpha_2\delta_M}}\right)\right) \tag{51}$$

$$\text{where } \alpha_2 = \frac{\dot{m}_o}{\rho D_{H_2O,eff}}\ . \tag{51a}$$

Note that the fluid phase flux through the membrane matrix is given by Eq. (31).

Assuming the fluid phase permeating through the membrane matrix to be consisted of H^+, water and methanol (neglecting dissolved species such as nitrogen, oxygen),

$$\sum_i x_i = 1 \tag{52}$$

where x_i is the mole fraction of species i. Therefore,

$$\left[\frac{c_{H^+}}{c_T} + \frac{c_{CH_3OH}}{c_T} + \frac{c_{H_2O}}{c_T} \right] = 1 \tag{52a}$$

where c_{H^+}, c_{CH_3OH}, c_{H_2O}, and c_T are the molar concentrations of H^+, methanol, water and fluid mixture, respectively. Here it is assumed that the fluid phase total molar concentration is constant throughout the membrane matrix. Differentiating Eq. (52a) leads to

$$\left(\frac{dc_{H^+}}{dx} \right) = -\frac{d}{dx}\left(c_{CH_3OH} + c_{H_2O} \right)$$

$$= -\left[\frac{dc_{CH_3OH}}{dx} + \frac{dc_{H_2O}}{dx} \right] \tag{53}$$

Using the expressions from Eqs. (49a) and (49b) in Eq. (53), the following expression for $\left(\frac{dc_{H^+}}{dx} \right)$ is obtained.

$$\left(\frac{dc_{H^+}}{dx} \right) = -\left[\begin{array}{l} \left(c^M_{CH_3OH,x=0} - c^M_{CH_3OH,x=\delta_M} \right) \left(\frac{\alpha_1 e^{\alpha_1 x}}{1 - e^{\alpha_1 \delta_M}} \right) \\ + \left(c^M_{H_2O,x=0} - c^M_{H_2O,x=\delta_M} \right) \left(\frac{\alpha_2 e^{\alpha_2 x}}{1 - e^{\alpha_2 \delta_M}} \right) \end{array} \right] \tag{54}$$

From Eq. (52a),

$$c^M_{H^+} = c_T - \left(c^M_{CH_3OH} + c^M_{H_2O} \right) \tag{55}$$

Applying this equation at x = 0 (membrane –anode interface) and at x = δ_M (membrane-cathode interface), the following expressions for $c^M_{H^+,x=0}$ and $c^M_{H^+,x=\delta_M}$ are obtained.

$$c^{M}_{H^+,x=0} = c_T - \left(c^{M}_{CH_3OH,x=0} + c^{M}_{H_2O,x=0}\right) \quad (56a)$$

$$c^{M}_{H^+,x=\delta_M} = c_T - \left(c^{M}_{CH_3OH,x=\delta_M} + c^{M}_{H_2O,x=\delta_M}\right) \quad (56b)$$

Then, the average concentration of hydrogen ion $\bar{c}_{H^+}$ in the membrane matrix (see Eq. 26) is given as

$$\bar{c}_{H^+} = \frac{c^{A}_{H^+} + c^{C}_{H^+}}{2} = \frac{c^{M}_{H^+,x=0} + c^{M}_{H^+,x=\delta_M}}{2} \quad (57a)$$

$$\bar{c}_{H^+} = c_T - \left(\frac{c^{M}_{CH_3OH,x=0} + c^{M}_{CH_3OH,x=\delta_M}}{2} + \frac{c^{M}_{H_2O,x=0} + c^{M}_{H_2O,x=\delta_M}}{2}\right) \quad (57b)$$

The methanol and water concentrations in the membrane at the membrane-porous electrode interfaces are to be computed from the concentrations of these species in the porous electrodes as shown in Eqs. (45) and (46).

The hydrogen ion concentration, $c^{M}_{H^+}$ in the membrane as a function of distance can be calculated using the Eqs. (45), (46), (54) and (55).

From Eqs. (29a) and (30),

$$\frac{d\Phi}{dx} = \frac{-\left|\Phi^C - \Phi^A\right|}{\delta_M} + \left(\frac{z_{H^+}\bar{c}_{H^+}F}{2\in}\right)\left(\delta_M - 2x\right) \quad (58)$$

$$\left(\frac{dp}{dx}\right) = -\left(\frac{\dot{m}_o\mu}{k_{pfM}\bar{\rho}}\right) - z_{H^+}\bar{c}_{H^+}F\left[\frac{-\left|\Phi^C - \Phi^A\right|}{\delta_M} + \frac{z_{H^+}\bar{c}_{H^+}F\delta_M}{2\in}\left(1 - \frac{2x}{\delta_M}\right)\right] \quad (59)$$

Now, $\left(\frac{dc_{H^+}}{dx}\right)_{@x=0}$, $\left(\frac{d\Phi}{dx}\right)_{@x=0}$, $\left(\frac{dp}{dx}\right)_{@x=0}$ are expressed as follows from, Eqs. (54), (58), and (59),

$$\left(\frac{dc_{H^+}}{dx}\right)_{@x=0} = -\left[\begin{array}{l}\left(c^{M}_{CH_3OH,x=0} - c^{M}_{CH_3OH,x=\delta_M}\right)\dfrac{\alpha_1}{1-e^{\alpha_1\delta_M}} \\ +\left(c^{M}_{H_2O,x=0} - c^{M}_{H_2O,x=\delta_M}\right)\dfrac{\alpha_2}{1-e^{\alpha_2\delta_M}}\end{array}\right] \quad 60)$$

$$\left(\frac{d\Phi}{dx}\right)_{@x=0} = \frac{-\left|\Phi^C - \Phi^A\right|}{\delta_M} + \left(\frac{z_{H^+}\bar{c}_{H^+}F}{2\in}\right)\delta_M \quad (61)$$

$$\left(\frac{dp}{dx}\right)_{@x=0} = -\left(\frac{\dot{m}_o \mu}{k_{pfM}\,\overline{\rho}}\right) - z_{H^+}\,\overline{c}_{H^+}\,F\left[\frac{-\left|\Phi^C - \Phi^A\right|}{\delta_M} + \frac{z_{H^+}\,\overline{c}_{H^+}\,F\,\delta_M}{2\in}\right] \tag{62}$$

Because of the steady-state condition, the following equations are obtained using Eqs. (17a) and (21):

$$\dot{N}_{H^+,x} = \dot{N}_{H^+,x=0} = \left[\left(\frac{z_{H^+}F}{RT}\right)D_{H^+,eff}\left(c^M_{H^+}\right)_{@\,x=0} + \left(\frac{k_{pfM}}{\mu}\right)z_{H^+}F\left(c^M_{H^+}\right)^2_{@\,x=0}\right]$$
$$*\left(\frac{\left|\Phi^C - \Phi^A\right|}{\delta_M} - \left(\frac{z_{H^+}\,\overline{c}_{H^+}F}{2\in}\right)\delta_M\right) + D_{H^+,eff}\left[\begin{array}{l}\left(c^M_{CH_3OH,x=0} - c^M_{CH_3OH,x=\delta_M}\right)\dfrac{\alpha_1}{1-e^{\alpha_1\delta_M}} \\ +\left(c^M_{H_2O,x=0} - c^M_{H_2O,x=\delta_M}\right)\dfrac{\alpha_2}{1-e^{\alpha_2\delta_M}}\end{array}\right] +$$
$$\left(\frac{k_{pfM}}{\mu}\right)\left(c_{H^+}\right)_{@\,x=0}\left(\left(\frac{\dot{m}_o\mu}{k_{pfM}\,\overline{\rho}}\right) + z_{H^+}\,\overline{c}_{H^+}F\left(\frac{-\left|\Phi^C - \Phi^A\right|}{\delta_M} + \frac{z_{H^+}\,\overline{c}_{H^+}F\delta_M}{2\in}\right)\right)$$

(63)

$$j_x = \left(j_x\right)_{@\,x=0} = \left(\frac{z^2_{H^+}F^2D_{H^+,eff}}{RT}\right)\left(c^M_{H^+}\right)_{@\,x=0}\left(-\frac{d\Phi}{dx}\right)_{@x=0}$$
$$+\left(\frac{k_{pfM}}{\mu}\right)\left(z_{H^+}\left(c^M_{H^+}\right)_{@\,x=0}F\right)^2\left(-\frac{d\Phi}{dx}\right)_{@x=0}$$
$$+\,z_{H^+}F\,D_{H^+,eff}\left(-\frac{dc_{H^+}}{dx}\right)_{@x=0}$$
$$+\left(\frac{k_{pfM}}{\mu}\right)\left(z_{H^+}\left(c^M_{H^+}\right)_{@\,x=0}F\right)\left(-\frac{dp}{dx}\right)_{@x=0} \tag{64}$$

$$j_x = \left(j_x\right)_{@\,x=0} = \left(\frac{z^2_{H^+}F^2D_{H^+,eff}}{RT}\right)\left(c^M_{H^+}\right)_{@\,x=0}\left[\frac{\left|\Phi^C - \Phi^A\right|}{\delta_M} - \frac{(z_{H^+}\,\overline{c}_{H^+}F)}{2\in}\delta_M\right]$$

$$+\left(\frac{k_{pfM}}{\mu}\right)\left(z_{H^+}\left(c^M_{H^+}\right)_{@\,x=0}F\right)^2\left[\frac{\left|\Phi^C-\Phi^A\right|}{\delta_M}-\frac{(z_{H^+}\bar{c}_{H^+}F)}{2\in}\delta_M\right]$$

$$+z_{H^+}FD_{H^+,eff}\begin{bmatrix}\left(c^M_{CH_3OH,x=0}-c^M_{CH_3OH,x=\delta_M}\right)\dfrac{\alpha_1}{1-e^{\alpha_1\delta_M}}\\ +\left(c^M_{H_2O,x=0}-c^M_{H_2O,x=\delta_M}\right)\dfrac{\alpha_2}{1-e^{\alpha_2\delta_M}}\end{bmatrix}$$

$$+\left(\frac{k_{pfM}}{\mu}\right)\left(z_{H^+}F\left(c^M_{H^+}\right)_{@\,x=0}\right)$$

$$*\left[\frac{\dot{m}_o\mu}{k_{pfM}\bar{\rho}}+\left(z_{H^+}\bar{c}_{H^+}F\right)\left(-\frac{\left|\Phi^C-\Phi^A\right|}{\delta_M}+\frac{(z_{H^+}\bar{c}_{H^+}F)\delta_M}{2\in}\right)\right] \qquad (65)$$

Note that $\alpha_1=\dfrac{\dot{m}_o}{\rho D_{CH_3OH,eff}}$; $\alpha_2=\dfrac{\dot{m}_o}{\rho D_{H_2O,eff}}$.

Also, $\bar{c}_{H^+}=\bar{c}^M_{H^+}$ is to be obtained from Eq. (57b), and $\left(c^M_{H^+}\right)_{@\,x=0}$ is to be obtained from Eq. (56a). Of course, $\dot{m}_o$ is to be obtained from Eq. (31).

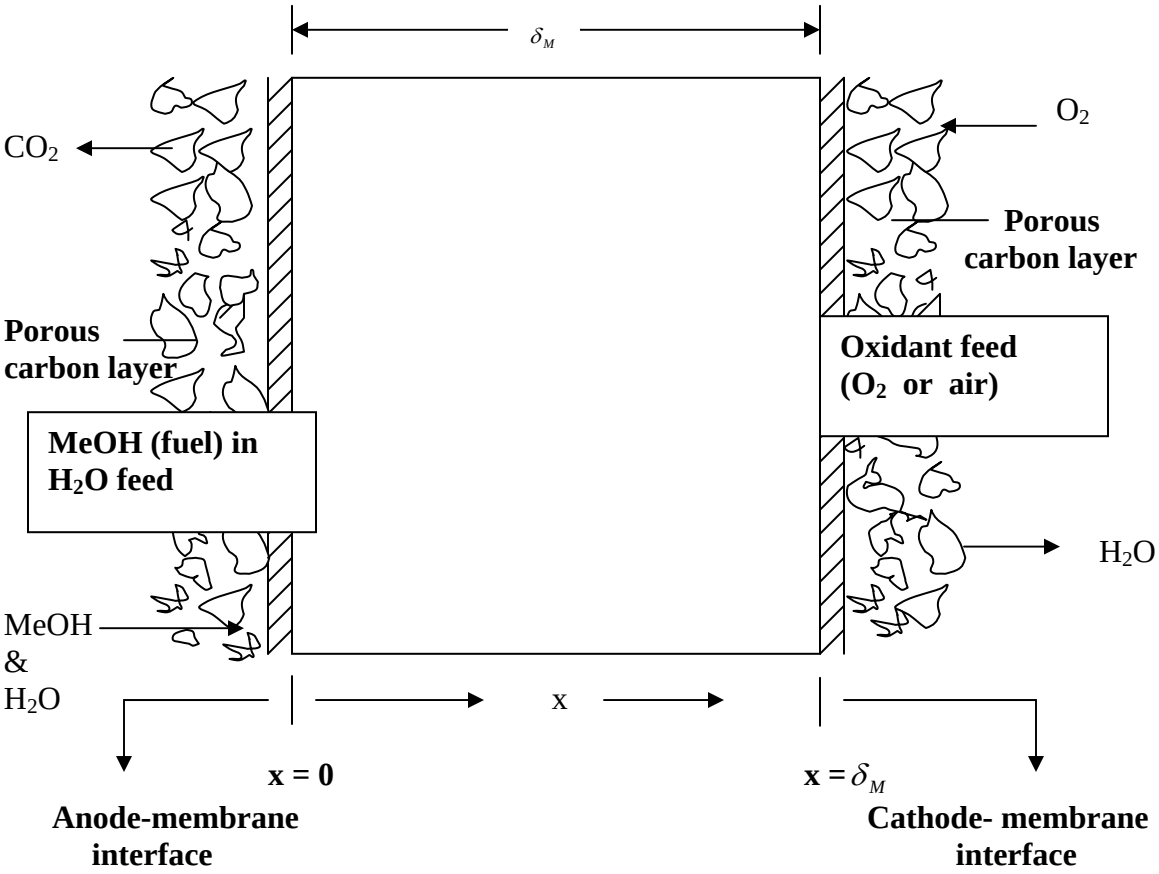
Equations (63) and (65) can be used to compute the hydrogen ion flux and current density, respectively, through the fluid phase in the membrane matrix.

4.1.2 Transport Set II Flux Equations using Maxwell-Stefan Relations

4.1.2.1 Introduction

An extremely wide variety of membrane types exist. One may distinguish between biological and synthetic membranes. Each type has wide range of composition and behavior. The synthetic membranes may be classified into (a) “homogenous”, (b) “microporous” and (c) mixtures of these two types. In a homogenous membrane the matrix plays the role of a true solvent for permeating species. The permeating species are confined to matrix-free regions in microporous membranes. These aspects are important for materials viewpoint. However, the formalisms needed to explain the transport of

species through them is much the same. Also note that the membranes are used in a wide range of process conditions.



Legend:

x = spatial coordinate

δ_M **= thickness of the membrane**

Figure 1. Polymer electrolyte membrane separating the porous anode and cathode layers (sketch not to scale).

4.1.2.2 Mathematical Derivation

The species transport equations given below are quite general in that they can be applied to any type of membrane (for example, acid doped polybenzimidazole, *Nafion*®, a

ceramic (clay: $Al_2O_3.2SiO_2.2H_2O$)- *Nafion*® or PVDF (polyvinylidene floride) composite). It is here assumed that the geometrical configuration of the membrane is invariant during the isothermal, steady-state operation of the direct methanol fuel cell (DMFC).

Here a membrane is viewed as an insoluble selectively permeable matrix M and one or more mobile permeating species; $\alpha, \beta, \ldots$. The membrane is defined here as having negligible curvature, i.e., its thickness is much less than its surface radius of curvature. This, in turn, implies that the mass transport is uni-directional and perpendicular to the membrane surface. The membrane matrix is immobile. That is, the velocity of the matrix is zero with regard to a stationary laboratory coordinate system. Velocities of the mobile species are referred to the coordinate system fixed in the stationary membrane. The diffusional response times within the membrane are assumed to be short in comparison with those in the mixtures in contact with its boundaries (located at x = 0 and x = δ as shown in the sketch; where δ is the thickness of the membrane). This effectively means that for every species a pseudosteady state prevails in the membrane even when slow transient conditions prevail in the mixtures in contact with its boundaries.

The Maxwell-Stefan equations given below satisfy the above mentioned membrane constraints and are specialized to generate reliable and compact descriptions of multicomponent transport in the membrane located between the electrodes of a direct methanol fuel cell.

It is recognized that the matrix is one of the components of the mixture of matrix, M and other electrochemical/chemical species such as H^+, CH_3OH, H_2O, etc. The Maxwell-Stefan equations are applied only for the mobile species (Ref. Bird et al.[2002]). From a thermodynamic viewpoint, we are concerned with the number of independent mobile components in the mixture bathing the membrane because it is the external solution that determines the equilibrium state of the membrane. As mentioned in the above reference,

determination of the effective molecular weight of the membrane matrix is very difficult for most situations, the internal system is defined to include only the mobile species and their mole fractions are defined to sum to unity. However, this restriction may be relaxed if the average molecular weight of the membrane material and its actual membrane material, M, mass density for its configuration between the fuel cell electrodes is known. The interaction of each mobile species with the membrane material, M, is quite significant; particularly, in the case of a membrane with the interstices of nanometer scale or less. Therefore, the modified mass diffusivity parameter associated with diffusion of a species α accounting for its interaction with the membrane is defined as

$$\frac{1}{Đ'_{\alpha M}} = \frac{x_M}{Đ_{\alpha M}} \tag{66}$$

where x_M, $Đ_{\alpha M}$ are the membrane material mole fraction and mass diffusivity of the component α through membrane, M; as it appears in the Maxwell-Stefan equations without excluding the membrane material; respectively. The generalized set of the Maxwell-Stefan equations for the fuel cell application is:

$$\sum_{\substack{\beta=1 \\ \neq\alpha}}^{allspecies} \frac{x_\alpha x_\beta}{Đ_{\alpha\beta}} \left(\vec{v}_\alpha - \vec{v}_\beta\right) = -x_\alpha \vec{\nabla} \ln a_\alpha - x_\alpha \left(\frac{\bar{v}_\alpha}{RT}\right) \vec{\nabla} p - x_\alpha z_\alpha \left(\frac{F}{RT}\right) \vec{\nabla}\Phi \tag{67}$$

(Here α = mobile species only = H^+, CH_3OH, H_2O only)

Note that according to the procedures used in the reference mentioned above, equation (67) should be used for the species that are mobile and permeate through the membrane. However, sum on the left-side of Eq. (67) should be carried over all species including the membrane matrix, M. In the event of that mole fraction of the membrane matrix M cannot be determined with a reasonable accuracy, it has been suggested, in the reference given above that $\frac{x_M}{Đ_{\alpha M}}$ be replaced by $\frac{1}{Đ'_{\alpha M}}$ in Eq.(67) and the species mole fractions be based on the mixture molar concentrations excluding the membrane matrix material.

In this equation, x_α, x_β are the mole fractions of the species α and β; $\vec{v}_\alpha$, $\vec{v}_\beta$, the resultant velocities of the species α and β, respectively; $Đ_{\alpha\beta}$, the diffusion coefficient

for the interaction of species α with the species β ; $\bar{v}_\alpha$, the partial molar volume of species α in the membrane ; $a_\alpha (= \gamma_\alpha x_\alpha)$; activity of the species α , here γ_α is the activity coefficient of the species α to account for the nonideal thermodynamic behavior of the 'membrane solution mixture' ; p, the thermodynamic pressure ; Φ , the electrostatic potential [volts]; z_α = number of positive or negative charges on a particle (i.e. number of charges on an ion), note that z_α for a charge neutral species is zero; R, the gas constant = 8.314 J/mol-K; T, the absolute temperature [K] ; F = Faraday's constant = 96487 Coulomb per gram- equivalent, i.e., 96487 Coulombs of charge on 1 gm-mole of unity charged particles such as H^+ ions or e^- electrons.

Equations (67) for the various mobile species are rewritten as:

$$\sum_{\substack{\beta=1 \\ \neq\alpha}}^{allspecies} \frac{x_\alpha x_\beta}{Đ_{\alpha\beta}} \left(\vec{v}_\alpha - \vec{v}_\beta\right) = - x_\alpha \left[\vec{\nabla} \ln a_\alpha + \frac{\bar{v}_\alpha}{RT} \vec{\nabla} p + z_\alpha \left(\frac{F}{RT} \right) \vec{\nabla} \Phi \right] \qquad (68)$$

(applied for α = H^+, CH_3OH, H_2O, etc.)

Note that terms within the brackets are the driving potentials for the transport of a species α through the membrane. For the assumption of the incompressible solute (H^+, CH_3OH, H_2O) in the membrane phase and system (i.e. membrane phase) isothermality, Eq. (68) can be written as:

$$\sum_{\substack{\beta=1 \\ \neq\alpha}}^{allspecies} \frac{x_\alpha x_\beta}{Đ_{\alpha\beta}} \left(\vec{v}_\alpha - \vec{v}_\beta\right) = - x_\alpha \left[\vec{\nabla} \left(\ln a_\alpha + \frac{p \bar{v}_\alpha}{RT} + \frac{z_\alpha F \Phi}{RT} \right) \right] \qquad (69)$$

(α = H^+, CH_3OH, H_2O)

The expression within the parentheses plays the role of "total potential" or driving force for the transport of a species α at any spatial point in the membrane phase.

The general boundary conditions are set up by requiring the "total potential" for each species α to be continuous across the boundary:

At x = 0, the anode-side boundary of the membrane in contact with the anode:

$$\left[\ln a_\alpha + \frac{p\bar{v}_\alpha}{RT} + \frac{z_\alpha F\Phi}{RT}\right]_{\substack{@\ x=0,A \\ (anode\ side)}} = \left[\ln a_\alpha + \frac{p\bar{v}_\alpha}{RT} + \frac{z_\alpha F\Phi}{RT}\right]_{\substack{@\ x=0,M \\ (membrane\ side)}} \quad (70a)$$

(for species α)

This equation is simplified to:

$$\left(\ln a_{\alpha,o,M} - \ln a_{\alpha,o,A}\right) + \left(\frac{\bar{v}_\alpha}{RT}\right)\left(p_{o,M} - p_{o,A}\right) + \left(\frac{z_\alpha F}{RT}\right)\left(\Phi_{o,M} - \Phi_{o,A}\right) = 0$$

$$\ln\left(\frac{a_{\alpha,o,M}}{a_{\alpha,o,A}}\right) + \left(\frac{\bar{v}_\alpha}{RT}\right)\left(p_{o,M} - p_{o,A}\right) + \left(\frac{z_\alpha F}{RT}\right)\left(\Phi_{o,M} - \Phi_{o,A}\right) = 0 \quad (70b)$$

(α = H^+, CH_3OH, H_2O)

A simplification results if the assumption of chemical equilibrium across the anode-membrane interface is valid,

i.e., $a_{\alpha,o,M} = a_{\alpha,o,A}$:

$$\left(\frac{\bar{v}_\alpha}{RT}\right)\left(p_{o,M} - p_{o,A}\right) + \left(\frac{z_\alpha F}{RT}\right)\left(\Phi_{o,M} - \Phi_{o,A}\right) = 0 \quad (70c)$$

Equations (70b) and (70c) may be written as:

$$\left[\ln a_{\alpha,o,M} + \left(\frac{\bar{v}_\alpha}{RT}\right)p_{o,M} + \frac{z_\alpha F}{RT}\Phi_{o,M}\right] = \left[\ln a_{\alpha,o,A} + \left(\frac{\bar{v}_\alpha}{RT}\right)p_{o,A} + \frac{z_\alpha F}{RT}\Phi_{o,A}\right] \quad (70d)$$

(α = H^+, CH_3OH, H_2O)

Also,

$$\left[\left(\frac{\bar{v}_\alpha}{RT}\right)p_{o,M} + \frac{z_\alpha F}{RT}\Phi_{o,M}\right] = \left[\left(\frac{\bar{v}_\alpha}{RT}\right)p_{o,A} + \frac{z_\alpha F}{RT}\Phi_{o,A}\right] \quad (70e)$$

(α = H^+, CH_3OH, H_2O)

For the one (x-) dimensional case, Eq. (69) becomes

$$\sum_{\substack{\beta=1 \\ \neq\alpha}}^{all\ species} \frac{x_\alpha x_\beta}{Đ_{\alpha\beta}}\left(v_\alpha - v_\beta\right)\vec{\delta}_x = -x_\alpha\left[\vec{\delta}_x \frac{d}{dx}\left(\ln a_\alpha + \frac{p\bar{v}_\alpha}{RT} + \frac{z_\alpha F\Phi}{RT}\right)\right] \quad (71)$$

$$\sum_{\substack{\beta=1 \\ \neq\alpha}}^{all\ species} \frac{x_\alpha x_\beta}{Đ_{\alpha\beta}}\left(v_\alpha - v_\beta\right) = -x_\alpha \frac{d}{dx}\left(\ln a_\alpha + \frac{p\bar{v}_\alpha}{RT} + \frac{z_\alpha F\Phi}{RT}\right) \quad (71a)$$

If c = total mixture concentration in the membrane phase, Eq. (71a) is rewritten as

$$\sum_{\substack{\beta=1 \\ \neq\alpha}}^{all\ species} \frac{(cx_\alpha)(cx_\beta)}{c^2 Đ_{\alpha\beta}}(v_\alpha - v_\beta) = -x_\alpha \frac{d}{dx}\left(\ln a_\alpha + \frac{p\bar{v}_\alpha}{RT} + \frac{z_\alpha F\Phi}{RT}\right) \qquad (71b)$$

$$\sum_{\substack{\beta=1 \\ \neq\alpha}}^{\beta=all}\left[\frac{c_\alpha c_\beta (v_\alpha - v_\beta)}{c^2 Đ_{\alpha\beta}}\right] = -x_\alpha \frac{d}{dx}\left(\ln a_\alpha + \frac{p\bar{v}_\alpha}{RT} + \frac{z_\alpha F\Phi}{RT}\right)$$

$$\sum_{\substack{\beta=1 \\ \neq\alpha}}^{\beta=all}\left[\frac{(c_\alpha v_\alpha)c_\beta - (c_\beta v_\beta)c_\alpha}{c^2 Đ_{\alpha\beta}}\right] = -x_\alpha \frac{d}{dx}\left(\ln a_\alpha + \frac{p\bar{v}_\alpha}{RT} + \frac{z_\alpha F\Phi}{RT}\right)$$

$$\sum_{\substack{\beta=1 \\ \neq\alpha}}^{\beta=all}\left[\frac{N_\alpha c_\beta - N_\beta c_\alpha}{c^2 Đ_{\alpha\beta}}\right] = -x_\alpha \frac{d}{dx}\left(\ln a_\alpha + \frac{p\bar{v}_\alpha}{RT} + \frac{z_\alpha F\Phi}{RT}\right)$$

$$\sum_{\substack{\beta=1 \\ \neq\alpha}}^{\beta=all}\left[\frac{N_\alpha c_\beta - N_\beta c_\alpha}{c\, Đ_{\alpha\beta}}\right] = -c_\alpha \frac{d}{dx}\left(\ln a_\alpha + \frac{p\bar{v}_\alpha}{RT} + \frac{z_\alpha F\Phi}{RT}\right) \qquad (72)$$

(α = H^+, CH_3OH, H_2O)

where N_α = molar flux of species α along x-direction at any point in the membrane phase.

Now, apply Eq. (72) to H^+, CH_3OH, H_2O :

First for $\alpha = H^+$:

$$\sum_{\substack{\beta=1 \\ \neq H^+}}^{\beta=all}\left[\frac{N_{H^+} c_\beta - N_\beta c_{H^+}}{c\, Đ_{H^+\beta}}\right] = -c_{H^+} \frac{d}{dx}\left(\ln a_{H^+} + \frac{p\bar{v}_{H^+}}{RT} + \frac{z_{H^+} F\Phi}{RT}\right) \qquad (73a)$$

$$\left(\frac{N_{H^+} c_{CH_3OH} - c_{H^+} N_{CH_3OH}}{c\, Đ_{H^+-CH_3OH}}\right) + \left(\frac{N_{H^+} c_{H_2O} - c_{H^+} N_{H_2O}}{c\, Đ_{H^+-H_2O}}\right) + \left(\frac{N_{H^+} c_M - c_{H^+} N_M}{c\, Đ_{H^+-M}}\right) =$$

$$-c_{H^+} \frac{d}{dx}\left(\ln a_{H^+} + \frac{p\bar{v}_{H^+}}{RT} + \frac{z_{H^+} F\Phi}{RT}\right) \qquad (73b)$$

Simplify:

$$\left(\frac{N_{H^+} c_{CH_3OH}}{c\, Đ_{H^+-CH_3OH}} + \frac{N_{H^+} c_{H_2O}}{c\, Đ_{H^+-H_2O}} + \frac{N_{H^+} c_M}{c\, Đ_{H^+-M}}\right) - \left(\frac{c_{H^+}}{c}\right)\left(\frac{N_{CH_3OH}}{Đ_{H^+-CH_3OH}} + \frac{N_{H_2O}}{Đ_{H^+-H_2O}}\right) =$$

$$- c_{H^+} \frac{d}{dx}\left(\ln a_{H^+} + \frac{p\bar{v}_{H^+}}{RT} + \frac{z_{H^+} F\Phi}{RT} \right) \qquad (73c)$$

$$N_{H^+}\left(\frac{c_{CH_3OH}}{c\,Đ_{H^+-CH_3OH}} + \frac{c_{H_2O}}{c\,Đ_{H^+-H_2O}} + \frac{c_M}{c\,Đ_{H^+-M}} \right) - \left(\frac{c_{H^+}}{c} \right)\left[\frac{N_{CH_3OH}}{Đ_{H^+-CH_3OH}} + \frac{N_{H_2O}}{Đ_{H^+-H_2O}} \right] =$$

$$c_{H^+}\left[-\frac{d}{dx}\left(\ln a_{H^+} + \frac{p\bar{v}_{H^+}}{RT} + \frac{F}{RT}\Phi \right) \right] \qquad (73d)$$

$$N_{H^+}\left(\frac{\left[c_{CH_3OH} / c_{H^+}\right]}{c\,Đ_{H^+-CH_3OH}} + \frac{\left[c_{H_2O} / c_{H^+}\right]}{c\,Đ_{H^+-H_2O}} + \frac{\left[c_M / c_{H^+}\right]}{c\,Đ_{H^+-M}} \right) - \left[\frac{N_{CH_3OH}}{c\,Đ_{H^+-CH_3OH}} + \frac{N_{H_2O}}{c\,Đ_{H^+-H_2O}} \right] =$$

$$-\frac{d}{dx}\left(\ln a_{H^+} + \frac{p\bar{v}_{H^+}}{RT} + \frac{F}{RT}\Phi \right) \qquad (74)$$

$$N_{H^+}\left(\frac{\frac{1}{c}\left[c_{CH_3OH} / c_{H^+}\right]}{Đ_{H^+-CH_3OH}} + \frac{\frac{1}{c}\left[c_{H_2O} / c_{H^+}\right]}{Đ_{H^+-H_2O}} + \frac{\left[\frac{1}{c}\left(c_M / c_{H^+}\right)\right]}{Đ_{H^+-M}} \right) - \left[\frac{N_{CH_3OH}}{c\,Đ_{H^+-CH_3OH}} + \frac{N_{H_2O}}{c\,Đ_{H^+-H_2O}} \right] =$$

$$-\frac{d}{dx}\left(\ln a_{H^+} + \frac{p\bar{v}_{H^+}}{RT} + \frac{F}{RT}\Phi \right) \qquad (74a)$$

Now, first we write the flux equations for methanol and water; we then come back to Eq.(74a). Say, α = CH_3 OH in Eq. (72):

$$\sum_{\substack{\beta=1 \\ \neq CH_3OH}}^{\beta=all} \left[\frac{N_{CH_3OH}\, c_\beta - c_{CH_3OH}\, N_\beta}{c\,Đ_{CH_3OH-\beta}} \right] = - c_{CH_3OH} \frac{d}{dx}\left(\ln a_{CH_3OH} + \frac{p\bar{v}_{CH_3OH}}{RT} + \frac{z_{CH_3OH}\, F}{RT}\Phi \right)$$

$$\frac{N_{CH_3OH}\, c_{H_2O} - c_{CH_3OH}\, N_{H_2O}}{c\,Đ_{CH_3OH-H_2O}} + \frac{N_{CH_3OH}\, c_{H^+} - c_{CH_3OH}\, N_{H^+}}{c\,Đ_{CH_3OH-H^+}} + \frac{N_{CH_3OH}\, c_M - c_{CH_3OH}\, N_M}{c\,Đ_{CH_3OH-M}} =$$

$$-c_{CH_3OH}\frac{d}{dx}\left(\ln a_{CH_3OH} + \frac{p\bar{v}_{CH_3OH}}{RT} \right)$$

$$N_{CH_3OH}\left[\frac{c_{H_2O}}{c\,Đ_{CH_3OH-H_2O}} + \frac{c_{H^+}}{c\,Đ_{CH_3OH-H^+}} + \frac{c_M}{c\,Đ_{CH_3OH-M}} \right] - \frac{c_{CH_3OH} N_{H^+}}{c\,Đ_{CH_3OH-H^+}} - \frac{c_{CH_3OH} N_{H_2O}}{c\,Đ_{CH_3OH-H_2O}} =$$

$$c_{CH_3OH}\left[-\frac{d}{dx}\left(\ln a_{CH_3OH} + \frac{p\bar{v}_{CH_3OH}}{RT} \right) \right]$$

Divide by c_{CH_3OH}:

$$N_{CH_3OH}\left[\frac{c_{H_2O}/c_{CH_3OH}}{c\,Đ_{CH_3OH-H_2O}}+\frac{c_{H^+}/c_{CH_3OH}}{c\,Đ_{CH_3OH-H^+}}+\frac{c_M/c_{CH_3OH}}{c\,Đ_{CH_3OH-M}}\right]-\left[\frac{N_{H^+}}{c\,Đ_{CH_3OH-H^+}}+\frac{N_{H_2O}}{c\,Đ_{CH_3OH-H^+}}\right]=$$

$$\left[-\frac{d}{dx}\left(\ln a_{CH_3OH}+\frac{p\bar{v}_{CH_3OH}}{RT}\right)\right] \qquad (74b)$$

Now, for $\alpha = H_2O$ in Eq. (72):

$$\sum_{\substack{\beta=1\\ \neq H_2O}}^{all}\left[\frac{N_{H_2O}\,c_\beta - c_{H_2O}\,N_\beta}{c\,Đ_{H_2O-\beta}}\right] = -c_{H_2O}\,\frac{d}{dx}\left(\ln a_{H_2O}+\frac{p\bar{v}_{H_2O}}{RT}+\frac{z_{H_2O}F}{RT}\Phi\right)$$

$$\frac{N_{H_2O}c_{H^+}-c_{H_2O}N_{H^+}}{c\,Đ_{H_2O-H^+}}+\frac{N_{H_2O}c_{CH_3OH}-c_{H_2O}N_{CH_3OH}}{c\,Đ_{H_2O-CH_3OH}}+\frac{N_{H_2O}c_M-c_{H_2O}N_M}{c\,Đ_{H_2O-M}} =$$

$$-c_{H_2O}\,\frac{d}{dx}\left(\ln a_{H_2O}+\frac{p\bar{v}_{H_2O}}{RT}\right)$$

$$N_{H_2O}\left(\frac{c_{H^+}}{c\,Đ_{H_2O-H^+}}+\frac{c_{CH_3OH}}{c\,Đ_{H_2O-CH_3OH}}+\frac{c_M}{c\,Đ_{H_2O-M}}\right)-\left(\frac{c_{H_2O}\,N_{H^+}}{c\,Đ_{H_2O-H^+}}+\frac{c_{H_2O}\,N_{CH_3OH}}{c\,Đ_{H_2O-CH_3OH}}\right)=$$

$$c_{H_2O}\left[-\frac{d}{dx}\left(\ln a_{H_2O}+\frac{p\bar{v}_{H_2O}}{RT}\right)\right] \qquad (74c)$$

At this stage, it is important to note that

$$Đ_{\alpha\beta} = Đ_{\beta\alpha} \qquad (75a)$$

(equivalent to the Onsagar reciprocal equation)

4.1.3 Transport Set III – Flux Equations using Onsager Thermodynamics

4.1.3.1 Introduction

The approach is based on the multicomponent diffusion using the Onsagar thermodyanamics as given in, "J.S. Newman, Electrochemical Systems, p.265, Prentice-Hall, 1991 edition." The membrane phase is assumed to be "homogenous" phase with the membrane matrix playing the role of a "true solvent" for the permeating species; H^+, CH_3OH and H_2O.

4.1.3.2 Mathematical Derivation

The starting, multicomponent diffusion equation for the transport of any species i is

$$c_i \vec{\nabla} \mu_i = \sum_j K_{ij} \left(\vec{v}_j - \vec{v}_i \right) = RT \sum_j \frac{c_i c_j}{c_T D_{ij}} \left(\vec{v}_j - \vec{v}_i \right) \qquad (76)$$

where c_i is the molar concentration of species i, c_T is the total concentration of the species including the solvent, R the universal gas constant, T the absolute temperature, μ_i the electrochemical potential of species i, K_{ij} the friction or interaction coefficients, D_{ij} the diffusion coefficient describing the interaction of species i and j. $\vec{v}_i$ is the average velocity of the species i but not the velocity of individual molecules. Equation (1) is similar to the Stefan-Maxwell equation [R.B.Bird, W.E.Stewart, and E.N. Lightfoot, Transport Phenomena, p.570, John Wiley and sons, Inc. New York, (1960)] and is equivalent to that developed by Onsagar [Lars Onsagar, "Theories and Problems of Liquid diffusion, "Annals of the New York Academy of Sciences, 46 (1945), pp.241-265].

The molar flux of species i is given by

$$\vec{N}_i = c_i \vec{v}_i \qquad (77)$$

The drag coefficients K_{ij} and diffusion coefficients D_{ij} are related as follows:

$$K_{ij} = \frac{RT c_i c_j}{c_T D_{ij}} \qquad (78)$$

Equation (1) can also be written as

$$c_i\left(-\vec{\nabla}\mu_i\right) = \sum_j K_{ij}\left(\vec{v}_i - \vec{v}_j\right) \qquad (79)$$

In this equation $K_{ij}\left(\vec{v}_i - \vec{v}_j\right)$ is the drag force exerted by species j on the species i because of the relative velocity difference. The sum on the right-side of Eq. (79) is the total drag force on the motion of species i per unit volume. The left-side of Eq. (79), $c_i\left(-\vec{\nabla}\mu_i\right)$ is regarded as a driving force per unit volume acting on species i. This force is considered to cause species i to move with respect to the surrounding fluid. Equation (79) expresses the balance between the driving force and the total drag exerted by the other species. By Newton's third law of motion, i.e., action is equal to reaction, $K_{ij} = K_{ji}$ or

$$D_{ij} = D_{ji} \quad \text{(Onsagar reciprocal relation)} \qquad (80)$$

It is noted here that the number of independent equations of the type (76) is one less than the number of species and adding them leads to:

$$\sum_i \left[c_i \vec{\nabla}\mu_i\right] = \sum_i \left[\sum_j K_{ij}\left(\vec{v}_j - \vec{v}_i\right)\right] \qquad (81)$$

The left side of Eq. (81) is zero as evidenced by the application of the Gibbs-Duhem equation at constant temperature and pressure [J.W.Tester, M.Modell, Thermodynamics and Its Applications, p.148, Prentice Hall, (1997 edition)]. The right side is zero because $K_{ij} = K_{ji}$.

Equation (76) is quite general because here the driving force on a species i is related to a linear combination of resistances opposing its motion instead of just one resistance relative to the solvent. The spatial gradient of the electrochemical potential acts as the driving force for diffusion and electric migration. The number of transport properties D_{ij} defined by Eq. (76) is $\left[n(n-1)/2\right]$ for n component system, because $D_{ij} = D_{ji}$ and D_{ii} is not defined; where n is the number of species involved.

For the membrane phase involving membrane matrix m, H^+, CH_3OH and H_2O; there are: 4(4-1)/2 = 6 transport properties of type D_{ij}.

Following Eq.(76)

$$c_i \vec{\nabla} \mu_i = \sum_j M_{ij} \left(\vec{v}_j - \vec{v}_m \right) \tag{82}$$

Where $\vec{v}_m$ = velocity of the membrane material which is zero in the current situation.

$$\sum_j M_{ij} \ \vec{v}_j = \quad c_i \vec{\nabla} \ \mu_i \tag{82a}$$

i = H^+, M, W; j = H^+, M, W, m;

$M_{ij} = K_{ij}$; $i \neq j$

$M_{ij} = K_{ij}$ - $\sum_k K_{ik}$; $i = j$; k = H^+, M, W, m.

Applied to $i = H^+$; M (CH_3OH); W (H_2O):

$$\sum_j M_{H^+ j} \ \vec{v}_j = c_{H^+} \vec{\nabla} \mu_{H^+} \tag{82b}$$

$$\sum_j M_{M j} \ \vec{v}_j = c_M \vec{\nabla} \mu_M \tag{82c}$$

$$\sum_j M_{W j} \ \vec{v}_j = c_W \vec{\nabla} \mu_W \tag{82d}$$

$$M_{H^+H^+} \ \vec{v}_{H^+} + M_{H^+M} \ \vec{v}_M + M_{H^+W} \ \vec{v}_W = c_{H^+} \vec{\nabla} \mu_{H^+} \tag{83a}$$

$$M_{MH^+} \ \vec{v}_{H^+} + M_{M\,M} \ \vec{v}_M + M_{M\,W} \ \vec{v}_W + M_{M\,m} \vec{v}_m = c_M \vec{\nabla} \mu_M \tag{83b}$$

$$M_{WH^+} \vec{v}_{H^+} + M_{W\,M} \ \vec{v}_M + M_{W\,W} \ \vec{v}_W + M_{W\,m} \vec{v}_m = c_W \vec{\nabla} \mu_W \tag{83c}$$

Note: No need to write an Eq. for membrane (m) species, because only, (n-1) = 4-1 = 3 independent Eqs. of the type (76) exist. Here $\vec{v}_m$ (membrane velocity) is zero (since membrane is assumed to be stationary with regard to the laboratory reference frame at the steady state conditions). So, Eqs.(83a) to (83c) become

$$M_{H^+H^+} \ \vec{v}_{H^+} + M_{H^+M} \ \vec{v}_M + M_{H^+W} \ \vec{v}_W = c_{H^+} \vec{\nabla} \mu_{H^+} \tag{83d}$$

$$M_{MH^+} \ \vec{v}_{H^+} + M_{M\,M} \ \vec{v}_M + M_{M\,W} \ \vec{v}_W = c_M \vec{\nabla} \mu_M \tag{83e}$$

$$M_{WH^+} \ \vec{v}_{H^+} + M_{W\,M} \ \vec{v}_M + M_{W\,W} \ \vec{v}_W = c_W \vec{\nabla} \mu_W \tag{83f}$$

With $i \neq j$

$M_{H^+M} = K_{H^+M}$; $M_{H^+W} = K_{H^+W}$; $M_{MH^+} = K_{MH^+}$;

$M_{MW} = K_{MW}$; $M_{WH^+} = K_{WH^+}$; $M_{WM} = K_{WM}$;

$$M_{H^+M} = M_{MH^+} = K_{MH^+} = K_{H^+M} \tag{84a}$$

$$M_{H^+W} = M_{WH^+} = K_{WH^+} = K_{H^+W} \tag{84b}$$

$$M_{MW} = M_{WM} = K_{WM} = K_{MW} \tag{84c}$$

For $i = j$

$$M_{ii} = K_{jj} - \sum_k K_{ik} \tag{85}$$

$i = H^+$:

$$M_{H^+H^+} = K_{H^+H^+} - \left[\sum_k K_{H^+k}\right] = K_{H^+H^+} - \left[K_{H^+H^+} + K_{H^+M} + K_{H^+W} + K_{H^+m}\right]$$

$$\therefore \quad M_{H^+H^+} = -\left(K_{H^+M} + K_{H^+W} + K_{H^+m}\right) \tag{85a}$$

i = M (CH_3OH):

$$M_{MM} = K_{MM} - \left[\sum_k K_{Mk}\right] = K_{MM} - \left[K_{MH^+} + K_{MM} + K_{MW} + K_{Mm}\right] \tag{85b}$$

$$M_{MM} = \left(K_{MH^+} + K_{MW} + K_{Mm}\right)$$

$$= -\left(K_{H^+M} + K_{MW} + K_{Mm}\right)$$

$i = W(H_2O)$:

$$M_{WW} = K_{WW} - \left[\sum_k K_{Wk}\right]$$

$$= K_{WW} - \left(K_{WH^+} + K_{WW} + K_{WM} + K_{Wm}\right)$$

$$M_{WW} = -\left(K_{WH^+} + K_{WM} + K_{Wm}\right) \tag{85c}$$

$$= -\left(K_{H^+W} + K_{WM} + K_{Wm}\right)$$

Note: Total interaction coefficients involved are:

$$\begin{pmatrix} K_{H^+M}, & K_{H^+W}, & K_{MW}; \\ K_{H^+m}, & K_{Mm}, & K_{Wm}. \end{pmatrix} \tag{86}$$

their # is = n(n-1)/2 = 4(4-1)/2 = 6

Three Eqs. (83), (83e), and (83f) are rewritten as

$$\begin{pmatrix} M_{H^+H^+} & M_{H^+M} & M_{H^+W} \\ M_{MH^+} & M_{MM} & M_{MW} \\ M_{WH^+} & M_{WM} & M_{WW} \end{pmatrix} \begin{pmatrix} \vec{v}_{H^+} \\ \vec{v}_M \\ \vec{v}_W \end{pmatrix} = \begin{pmatrix} c_{H^+}\vec{\nabla}\mu_{H^+} \\ c_M\vec{\nabla}\mu_M \\ c_W\vec{\nabla}\mu_W \end{pmatrix} \tag{87}$$

Call the matrix made of M's as L matrix, $\begin{pmatrix} \vec{v}_{H^+} \\ \vec{v}_M \\ \vec{v}_W \end{pmatrix}$ column vector as $\vec{V}$; and the one in

right-side as $\vec{D}$ driving force vector; Therefore we can write as

$$\text{L } \vec{V} = \vec{D} \tag{88}$$

If L is non-singular matrix, i.e., determinant (L) $\neq$ 0; so that L^{-1} (inverse of matrix L) exists, then Eq. (87) or (88) is solved by writing

$$\vec{V} = L^{-1}\vec{D} \tag{89}$$

(Advanced Mathematics by M.R. Spiegel, p.347 (1971 edition), 24th printing (1996))

The system of equations has unique solution.

For one (x-) dimensional case, Eq.(89) is written as

$$\vec{\delta}_x \, v_x = L^{-1}\vec{\delta}_x \, D_x \tag{89a}$$

or,

$$v_x = L^{-1} D_x \tag{89b}$$

where $v_x = \begin{pmatrix} v_{H^+,x} \\ v_{M,x} \\ v_{W,x} \end{pmatrix}$; $D_x = \begin{pmatrix} c_{H^+}\dfrac{d\mu_{H^+}}{dx} \\ c_M\dfrac{d\mu_M}{dx} \\ c_W\dfrac{d\mu_W}{dx} \end{pmatrix}$ (89c)

Note: Find L^{-1}, then get expressions for $v_{H^+,x}$, $v_{M,x}$ and $v_{W,x}$. Then, move on

$$L^{-1} = ?$$

$$\text{Matrix (L)} = \begin{pmatrix} M_{H^+H^+} & M_{H^+M} & M_{H^+W} \\ M_{MH^+} & M_{MM} & M_{MW} \\ M_{WH^+} & M_{WM} & M_{WW} \end{pmatrix} \tag{90}$$

Because $M_{H^+M} = M_{MH^+}$; $M_{WH^+} = M_{H^+W}$; $M_{WM} = M_{MW}$.

Note that the L matrix is the symmetric matrix.

The inverse matrix L^{-1} is defined as

$$(L^{-1}) = \frac{(M_{jk})^T}{\det(L)} \tag{91}$$

where det (L) = value of the determinant of the square matrix L, and (M_{jk}) is the matrix made of cofactors of the elements in the matrix L; $(M_{jk})^T$ is the transpose of (M_{jk}).

$(M_{jk}) =$

$$\begin{pmatrix} (-1)^{1+1}\begin{vmatrix} M_{MM} & M_{MW} \\ M_{MW} & M_{WW} \end{vmatrix} & (-1)^{1+2}\begin{vmatrix} M_{H^+M} & M_{MW} \\ M_{H^+W} & M_{WW} \end{vmatrix} & (-1)^{1+3}\begin{vmatrix} M_{H^+M} & M_{MM} \\ M_{H^+W} & M_{MW} \end{vmatrix} \\ (-1)^{2+1}\begin{vmatrix} M_{H^+M} & M_{H^+W} \\ M_{MW} & M_{WW} \end{vmatrix} & (-1)^{2+2}\begin{vmatrix} M_{H^+H^+} & M_{H^+W} \\ M_{H^+W} & M_{WW} \end{vmatrix} & (-1)^{2+3}\begin{vmatrix} M_{H^+H^+} & M_{H^+M} \\ M_{H^+W} & M_{MW} \end{vmatrix} \\ (-1)^{3+1}\begin{vmatrix} M_{H^+M} & M_{H^+W} \\ M_{MM} & M_{MW} \end{vmatrix} & (-1)^{3+2}\begin{vmatrix} M_{H^+H^+} & M_{H^+W} \\ M_{H^+M} & M_{MW} \end{vmatrix} & (-1)^{3+3}\begin{vmatrix} M_{H^+H^+} & M_{H^+M} \\ M_{H^+M} & M_{MM} \end{vmatrix} \end{pmatrix}$$

$(M_{jk}) =$

$$\begin{pmatrix} (M_{MM}M_{WW} - M_{MW}M_{MW}) & -(M_{H^+M}M_{WW} - M_{H^+W}M_{MW}) & (M_{H^+M}M_{MW} - M_{H^+W}M_{MM}) \\ -(M_{H^+M}M_{WW} - M_{MW}M_{H^+W}) & (M_{H^+H^+}M_{WW} - M_{H^+W}M_{H^+W}) & -(M_{H^+H^+}M_{MW} - M_{H^+M}M_{H^+W}) \\ (M_{H^+M}M_{MW} - M_{H^+W}M_{MM}) & -(M_{H^+H^+}M_{MW} - M_{H^+M}M_{H^+W}) & (M_{H^+H^+}M_{MM} - M_{H^+M}M_{H^+M}) \end{pmatrix}$$

$$\left(M_{jk}\right) =$$

$$\begin{pmatrix} \left(M_{MM}M_{WW} - M_{MW}^{2}\right) & \left(M_{H^{+}W}M_{MW} - M_{H^{+}M}M_{WW}\right) & \left(M_{H^{+}M}M_{MW} - M_{H^{+}W}M_{MM}\right) \\ \left(M_{MW}M_{H^{+}W} - M_{H^{+}M}M_{WW}\right) & \left(M_{H^{+}H^{+}}M_{WW} - M_{H^{+}W}^{2}\right) & \left(M_{H^{+}M}M_{H^{+}W} - M_{H^{+}H^{+}}M_{MW}\right) \\ \left(M_{H^{+}M}M_{MW} - M_{H^{+}W}M_{MM}\right) & \left(M_{H^{+}M}M_{H^{+}W} - M_{H^{+}H^{+}}M_{MW}\right) & \left(M_{H^{+}H^{+}}M_{MM} - M_{H^{+}M}^{2}\right) \end{pmatrix}$$

$$\left(M_{jk}\right)^{T} =$$

$$\begin{pmatrix} \left(M_{MM}M_{WW} - M_{MW}^{2}\right) & \left(M_{H^{+}W}M_{MW} - M_{H^{+}M}M_{WW}\right) & \left(M_{H^{+}M}M_{MW} - M_{H^{+}W}M_{MM}\right) \\ \left(M_{MW}M_{H^{+}W} - M_{H^{+}M}M_{WW}\right) & \left(M_{H^{+}H^{+}}M_{WW} - M_{H^{+}W}^{2}\right) & \left(M_{H^{+}M}M_{H^{+}W} - M_{H^{+}H^{+}}M_{MW}\right) \\ \left(M_{H^{+}M}M_{MW} - M_{H^{+}W}M_{MM}\right) & \left(M_{H^{+}M}M_{H^{+}W} - M_{H^{+}H^{+}}M_{MW}\right) & \left(M_{H^{+}H^{+}}M_{MM} - M_{H^{+}M}^{2}\right) \end{pmatrix}^{T}$$

$$\left(M_{jk}\right)^{T} =$$

$$\begin{pmatrix} \left(M_{MM}M_{WW} - M_{MW}^{2}\right) & \left(M_{MW}M_{H^{+}W} - M_{H^{+}M}M_{WW}\right) & \left(M_{H^{+}M}M_{MW} - M_{H^{+}W}M_{MM}\right) \\ \left(M_{H^{+}W}M_{MW} - M_{H^{+}M}M_{WW}\right) & \left(M_{H^{+}H^{+}}M_{WW} - M_{H^{+}W}^{2}\right) & \left(M_{H^{+}M}M_{H^{+}W} - M_{H^{+}H^{+}}M_{MW}\right) \\ \left(M_{H^{+}M}M_{MW} - M_{H^{+}W}M_{MM}\right) & \left(M_{H^{+}M}M_{H^{+}W} - M_{H^{+}H^{+}}M_{MW}\right) & \left(M_{H^{+}H^{+}}M_{MM} - M_{H^{+}M}^{2}\right) \end{pmatrix}$$

(92)

$$\left(M_{jk}\right)^{T} = \begin{pmatrix} M_{11} & M_{12} & M_{13} \\ M_{21} & M_{22} & M_{23} \\ M_{31} & M_{32} & M_{33} \end{pmatrix} \tag{93}$$

where $M_{11} = \left(M_{MM}M_{WW} - M_{MW}^{2}\right),$

$M_{12} = \left(M_{MW}M_{H^{+}W} - M_{H^{+}M}M_{WW}\right),$

$M_{13} = \left(M_{H^{+}M}M_{MW} - M_{H^{+}W}M_{MM}\right),$

$M_{21} = \left(M_{H^{+}W}M_{MW} - M_{H^{+}M}M_{WW}\right),$

$M_{22} = \left(M_{H^{+}H^{+}}M_{WW} - M_{H^{+}W}^{2}\right),$

$$M_{23} = \left(M_{H^+M} M_{H^+W} - M_{H^+H^+} M_{MW}\right),$$
$$M_{31} = \left(M_{H^+M} M_{MW} - M_{H^+W} M_{MM}\right),$$
$$M_{32} = \left(M_{H^+M} M_{H^+W} - M_{H^+H^+} M_{MW}\right),$$
$$M_{33} = \left(M_{H^+H^+} M_{MM} - M^2_{H^+M}\right).$$

(94)

The determinant of matrix (L) is

$$\text{Det (L)} = \begin{vmatrix} M_{H^+H^+} & M_{H^+M} & M_{H^+W} \\ M_{MH^+} & M_{MM} & M_{MW} \\ M_{WH^+} & M_{WM} & M_{WW} \end{vmatrix} \qquad (95)$$

The determinant det (L) is the 3rd order determinant .

From Eq. (91), (93), the inverse matrix (L^{-1}) is

$$(L^{-1}) = \left[\frac{\begin{pmatrix} M_{11} & M_{12} & M_{13} \\ M_{21} & M_{22} & M_{23} \\ M_{31} & M_{32} & M_{33} \end{pmatrix}}{\det(L)}\right]$$

$$= \frac{1}{\det(L)} \begin{pmatrix} M_{11} & M_{12} & M_{13} \\ M_{21} & M_{22} & M_{23} \\ M_{31} & M_{32} & M_{33} \end{pmatrix}$$

$$(L^{-1}) = \begin{pmatrix} \frac{M_{11}}{\det(L)} & \frac{M_{12}}{\det(L)} & \frac{M_{13}}{\det(L)} \\ \frac{M_{21}}{\det(L)} & \frac{M_{22}}{\det(L)} & \frac{M_{23}}{\det(L)} \\ \frac{M_{31}}{\det(L)} & \frac{M_{32}}{\det(L)} & \frac{M_{33}}{\det(L)} \end{pmatrix} \qquad (96)$$

We now use Eqs.(89b), (89c) and (96):

$$\begin{pmatrix} v_{H^+,x} \\ v_{M,x} \\ v_{W,x} \end{pmatrix} = \begin{pmatrix} \frac{M_{11}}{\det(L)} & \frac{M_{12}}{\det(L)} & \frac{M_{13}}{\det(L)} \\ \frac{M_{21}}{\det(L)} & \frac{M_{22}}{\det(L)} & \frac{M_{23}}{\det(L)} \\ \frac{M_{31}}{\det(L)} & \frac{M_{32}}{\det(L)} & \frac{M_{33}}{\det(L)} \end{pmatrix} \begin{pmatrix} c_{H^+} \frac{d\mu_{H^+}}{dx} \\ c_M \frac{d\mu_M}{dx} \\ c_W \frac{d\mu_W}{dx} \end{pmatrix}$$

$$\begin{pmatrix} v_{H^+,x} \\ v_{M,x} \\ v_{W,x} \end{pmatrix} = \begin{pmatrix} \left(\frac{M_{11}}{\det(L)}\right)\left(c_{H^+} \frac{d\mu_{H^+}}{dx}\right) + \left(\frac{M_{12}}{\det(L)}\right)\left(c_M \frac{d\mu_M}{dx}\right) + \left(\frac{M_{13}}{\det(L)}\right)\left(c_W \frac{d\mu_W}{dx}\right) \\ \left(\frac{M_{21}}{\det(L)}\right)\left(c_{H^+} \frac{d\mu_{H^+}}{dx}\right) + \left(\frac{M_{22}}{\det(L)}\right)\left(c_M \frac{d\mu_M}{dx}\right) + \left(\frac{M_{23}}{\det(L)}\right)\left(c_W \frac{d\mu_W}{dx}\right) \\ \left(\frac{M_{31}}{\det(L)}\right)\left(c_{H^+} \frac{d\mu_{H^+}}{dx}\right) + \left(\frac{M_{32}}{\det(L)}\right)\left(c_M \frac{d\mu_M}{dx}\right) + \left(\frac{M_{33}}{\det(L)}\right)\left(c_W \frac{d\mu_W}{dx}\right) \end{pmatrix}$$

(97)

Hence, equations for the "net" velocities of species H^+, M (methanol, CH_3OH), and W (water, H_2O) are given below:

$$v_{H^+,x} = \left(\left(\frac{M_{11}}{\det(L)}\right)\left(c_{H^+} \frac{d\mu_{H^+}}{dx}\right) + \left(\frac{M_{12}}{\det(L)}\right)\left(c_M \frac{d\mu_M}{dx}\right) + \left(\frac{M_{13}}{\det(L)}\right)\left(c_W \frac{d\mu_W}{dx}\right)\right)$$

$$v_{M,x} = \left(\left(\frac{M_{21}}{\det(L)}\right)\left(c_{H^+} \frac{d\mu_{H^+}}{dx}\right) + \left(\frac{M_{22}}{\det(L)}\right)\left(c_M \frac{d\mu_M}{dx}\right) + \left(\frac{M_{23}}{\det(L)}\right)\left(c_W \frac{d\mu_W}{dx}\right)\right)$$

$$v_{W,x} = \left(\left(\frac{M_{31}}{\det(L)}\right)\left(c_{H^+} \frac{d\mu_{H^+}}{dx}\right) + \left(\frac{M_{32}}{\det(L)}\right)\left(c_M \frac{d\mu_M}{dx}\right) + \left(\frac{M_{33}}{\det(L)}\right)\left(c_W \frac{d\mu_W}{dx}\right)\right)$$

(98)

Note: det(L) from Eqs.(90), [84a, b, c; 85a, b, c]

M's from Eq.(94), [84a, b, c], [85a, b, c]

We may write Eq.(98) as:

$$v_{H^+,x} = \frac{1}{\det(L)} \left(M_{11}\left(c_{H^+} \frac{d\mu_{H^+}}{dx}\right) + M_{12}\left(c_M \frac{d\mu_M}{dx}\right) + M_{13}\left(c_W \frac{d\mu_W}{dx}\right)\right)$$

$$v_{M,x} = \frac{1}{\det(L)} \left(M_{21}\left(c_{H^+} \frac{d\mu_{H^+}}{dx}\right) + M_{22}\left(c_M \frac{d\mu_M}{dx}\right) + M_{23}\left(c_W \frac{d\mu_W}{dx}\right)\right)$$

$$v_{W,x} = \frac{1}{\det(L)} \left(M_{31}\left(c_{H^+} \frac{d\mu_{H^+}}{dx} \right) + M_{32}\left(c_M \frac{d\mu_M}{dx} \right) + M_{33}\left(c_W \frac{d\mu_W}{dx} \right) \right) \tag{99}$$

Treatment of chemical potentials μ_i of the species:

For a charge neutral species,

$$\mu_i = \Omega_i(@T,P) + RT\ln(\gamma_i\, x_i) \tag{100}$$

where μ_i = chemical potential of a charge neutral species i in the membrane phase at any point,

$\Omega_i(@T,P)$ = chemical potential of species i as pure at the temperature T and pressure P and in the same state of aggregation as that of it in the "membrane solution phase",(may be assumed to be the liquid phase);

γ_i = activity coefficient of species i; it is a function of temperature, pressure and composition of the "membrane solution phase";

x_i = mole fraction of species i in the solution phase.

Note: Here, i = CH_3OH, H_2O, and the membrane material m if it is assumed charge neutral.

From (100),

$$d\mu_i = d\Omega_i + d\left[RT\ln(\gamma_i\, x_i)\right] \tag{101}$$

$$= \left(V_i dP - S_i dT\right) + d\left[RT\ln(\gamma_i\, x_i)\right] \tag{102}$$

$$d\mu_i = V_i dP - S_i dT + R\, d\left[T\ln(\gamma_i\, x_i)\right] \tag{103}$$

where V_i, S_i = molar volume and entropy of pure species i at (T,P) of the system at a spatial point in the membrane phase solution.

If the condition of isothermality is applied; Eq.(103) becomes

$$d\mu_i = V_i dP + R\, d\left[T\ln(\gamma_i\, x_i)\right] \tag{104}$$

divide by dx:

$$\left(\frac{d\mu_i}{dx}\right) = V_i \frac{dP}{dx} + RT \frac{d\ln(\gamma_i\, x_i)}{dx} \tag{105}$$

i = M (CH_3OH), W(H_2O), m (membrane material as a component).

Electrochemical potential of H^+ is defined as:

$$\mu_{H^+} = \mu_{H^+}^{chem} + z_{H^+} F \Phi \tag{106}$$

$$= \text{RT } \ln\left[\lambda_{H^+}^{\theta,chem} \gamma_{H^+} \frac{m_{H^+}}{m^o} \right] + z_{H^+} F \Phi \tag{106a}$$

where m^o = a reference molality (e.g. 1 g-mole per kg of a solvent).

The molality m_{H^+} is given also as:

$$m_{H^+} = \frac{c_{H^+}}{c_o M_o} \tag{106b}$$

$c_o M_o$ = solvent concentration in mass units, here solvent assumed to be mixture of the membrane material m, water, methanol; for the transport of H^+ ions. M_o is the molecular weight of the solvent.

The expression for m_{H^+} is rewritten as

$$m_{H^+} = \frac{\lfloor c_{H^+} / c_T \rfloor}{\left(\frac{c_o}{c_T} \right) M_o}$$

$$= \left(\frac{x_{H^+}}{x_o M_o} \right) \tag{106c}$$

where c_T = total mixture concentration and c_{H^+} = hydrogen ion concentration.

One may then say, x_o = 1- x_{H^+} , if all other species; membrane material (m), CH_3OH, H_2O are taken to constitute the solvent for H^+ ion transport.

Putting Eq. (106c) into (106):

$$\mu_{H^+} = RT \ln\left[\lambda_{H^+}^{\theta,chem} \gamma_{H^+} \frac{x_{H^+}}{x_o M_o m^o} \right] + z_{H^+} F \Phi \tag{106d}$$

$$= \left[RT \ln \lambda_{H^+}^{\theta,chem} \right] + \text{RT } \ln\left(\gamma_{H^+} \frac{x_{H^+}}{x_o} \right) - \text{RT } \ln\left(M_o m^o \right) + z_{H^+} F \Phi \tag{106e}$$

$$\therefore \left(\frac{d\mu_{H^+}}{dx}\right) = R\frac{d}{dx}\left[T\ln\lambda_{H^+}^{\theta,chem}\right] + R\frac{d}{dx}\left[T\ln\left(\gamma_{H^+}\frac{x_{H^+}}{x_o}\right)\right] - \mathrm{R}\ln\left(M_o m^o\right)\frac{dT}{dx} + z_{H^+}F\frac{d\Phi}{dx} \tag{106f}$$

Under the condition of constant temperature and assuming that the effect of pressure variation on $\lambda_{H^+}^{\theta,chem}$ across the membrane for the pressure variations of the order of 10 bar is negligibly small; then Eq.(106) reduces to:

$$\left(\frac{d\mu_{H^+}}{dx}\right) = 0 + RT\frac{d}{dx}\left[\ln\left(\gamma_{H^+}\frac{x_{H^+}}{x_o}\right)\right] - 0 + z_{H^+}F\frac{d\Phi}{dx}$$

$$= RT\frac{d}{dx}\left[\ln\left(\gamma_{H^+}\frac{x_{H^+}}{x_o}\right)\right] + z_{H^+}F\frac{d\Phi}{dx} \tag{106g}$$

$$\therefore \left(c_{H^+}\frac{d\mu_{H^+}}{dx}\right) = \left(c_{H^+}RT\right)\frac{d}{dx}\left[\ln\left(\gamma_{H^+}\frac{x_{H^+}}{x_o}\right)\right] + \left(c_{H^+}z_{H^+}\right)F\frac{d\Phi}{dx} \tag{106h}$$

$$= \left(c_{H^+}RT\right)\left[\frac{d}{dx}\left(\ln\gamma_{H^+} + \ln\frac{x_{H^+}}{x_o}\right)\right] + \left(c_{H^+}z_{H^+}\right)F\frac{d\Phi}{dx}$$

$$\left(c_{H^+}\frac{d\mu_{H^+}}{dx}\right) = \left(c_{H^+}RT\right)\left[\frac{d\ln\gamma_{H^+}}{dx} + \frac{d}{dx}\left(\ln\frac{x_{H^+}}{x_o}\right)\right] + \left(c_{H^+}z_{H^+}\right)F\frac{d\Phi}{dx} \tag{106i}$$

From Eq.(30)

$$\left(c_i\frac{d\mu_i}{dx}\right) = c_i V_i\frac{dP}{dx} + c_i RT\left[\frac{d\left(\ln\gamma_i\right)}{dx} + \frac{d\left(\ln x_i\right)}{dx}\right] \tag{106j}$$

where i = CH_3OH, H_2O.

Assuming γ_{H^+}, γ_i variation with x over the "membrane phase" negligibly small,

$\frac{d\ln\gamma_{H^+}}{dx} = \frac{d\ln\gamma_i}{dx} = 0$; then Eqs.(106i) and (106j) becomes:

$$\left(c_{H^+}\frac{d\mu_{H^+}}{dx}\right) = \left(c_{H^+}RT\right)\left[\frac{d}{dx}\left(\ln\frac{x_{H^+}}{x_o}\right)\right] + \left(c_{H^+}z_{H^+}\right)F\frac{d\Phi}{dx} \tag{107a}$$

$$\left(c_i\frac{d\mu_i}{dx}\right) = c_i V_i\frac{dP}{dx} + c_i RT\frac{d}{dx}\left[\ln x_i\right] \tag{107b}$$

Note: $\left[\frac{M_{ij}}{\det[L]}\right] = \left[\frac{1}{\left[\frac{J.s}{m^5}\right]}\right] = \left[\frac{m^5}{J.s}\right]$

So that $\left[\frac{M_{ij}}{\det[L]}\right]\left(c_i \frac{d\mu_i}{dx}\right) = \left[\frac{m^5}{J.s}.\frac{J}{m^4}\right] \equiv \left[\frac{m}{s}\right]$

Simplification:

If $\frac{dP}{dx} = 0$, if pressure on both sides of the membrane are same or if the effect of $\frac{dP}{dx}$ on the transport of a species is negligible; then (107b) becomes:

$$\left(c_i \frac{d\mu_i}{dx}\right) = c_i RT \frac{d \ln x_i}{dx} \qquad (108)$$

i = CH_3OH, H_2O.

$$\left(c_M \frac{d\mu_M}{dx}\right) = c_M RT \frac{d \ln x_M}{dx}$$

$$= c_M RT \frac{d \ln x_M}{dx_M}.\frac{dx_M}{dx}$$

$$= (x_M c_T)(RT).\frac{1}{x_M}\frac{dx_M}{dx} = (c_T RT)\frac{dx_M}{dx} \qquad (109a)$$

Also, $c_W \frac{d\mu_{H_2O}}{dx} = c_W RT \frac{d \ln x_W}{dx}$

$$= x_W c_T RT \frac{d \ln x_W}{dx_W}\frac{dx_W}{dx}$$

$$= (x_W c_T RT)\frac{1}{x_W}\frac{dx_W}{dx}$$

$$= (c_T RT)\left(\frac{dx_W}{dx}\right) \qquad (109b)$$

Also, $c_{H^+} \frac{d}{dx}\left[\ln\left(x_{H^+} / x_o\right)\right] = \left(x_{H^+} c_T\right)\frac{d}{dx}\left[\ln\left(x_{H^+} / x_o\right)\right]$

$$= \left(x_{H^+} c_T\right)\frac{d \ln\left(x_{H^+} / x_o\right)}{d\left(x_{H^+} / x_o\right)}\frac{d\left(x_{H^+} / x_o\right)}{dx}$$

$$= \left(x_{H^+} c_T\right) \frac{1}{\left(x_{H^+} / x_o\right)} \frac{d\left(x_{H^+} / x_o\right)}{dx}$$

$$= \left(x_{H^+} c_T\right)\left(\frac{x_o}{x_{H^+}}\right) \frac{d}{dx}\left(x_{H^+} / x_o\right) = \left(c_T x_o\right)\left[\frac{d\left(x_{H^+} / x_o\right)}{dx}\right]$$

$$= \left(c_T \frac{x_o}{x_o}\right)\left(\frac{dx_{H^+}}{dx}\right)$$

$$= \left(c_T\right)\left(\frac{dx_{H^+}}{dx}\right) \tag{110}$$

From (32a) and (35):

$$\left(c_{H^+} \frac{d\mu_{H^+}}{dx}\right) = \left(c_T RT\right)\left(\frac{dx_{H^+}}{dx}\right) + c_T z_{H^+} x_{H^+} F \frac{d\Phi}{dx} \tag{111}$$

$$= \left(c_T RT\right)\left(\frac{dx_{H^+}}{dx}\right) + c_T z_{H^+} F x_{H^+} \frac{d\Phi}{dx} \tag{111a}$$

Substitute from (109a), (109b), and (111a) into Eqs.(98):

$$v_{H^+,x} = \left(\frac{M_{11}}{\det(L)}\right)\left[\left(c_T RT\right)\frac{dx_{H^+}}{dx} + z_{H^+} c_T F x_{H^+} \frac{d\Phi}{dx}\right] +$$

$$\left(\frac{M_{12}}{\det(L)}\right)\left[\left(c_T RT\right)\frac{dx_M}{dx}\right] + \left(\frac{M_{13}}{\det(L)}\right)\left[\left(c_T RT\right)\frac{dx_W}{dx}\right] \tag{112a}$$

$$v_{M,x} = \left(\frac{M_{21}}{\det(L)}\right)\left[\left(c_T RT\right)\frac{dx_{H^+}}{dx} + z_{H^+} c_T F x_{H^+} \frac{d\Phi}{dx}\right] +$$

$$\left(\frac{M_{22}}{\det(L)}\right)\left[\left(c_T RT\right)\frac{dx_M}{dx}\right] + \left(\frac{M_{23}}{\det(L)}\right)\left[\left(c_T RT\right)\frac{dx_W}{dx}\right] \tag{112b}$$

$$v_{W,x} = \left(\frac{M_{31}}{\det(L)}\right)\left[\left(c_T RT\right)\frac{dx_{H^+}}{dx} + z_{H^+} c_T F x_{H^+} \frac{d\Phi}{dx}\right] +$$

$$\left(\frac{M_{32}}{\det(L)}\right)\left[\left(c_T RT\right)\frac{dx_M}{dx}\right] + \left(\frac{M_{33}}{\det(L)}\right)\left[\left(c_T RT\right)\frac{dx_W}{dx}\right] \tag{112c}$$

The molar fluxes of the species are given as:

$$N_{i,x} = V_{i,x} c_i \tag{113}$$

The continuity equation for a species i in the membrane phase, under the steady-state condition,

$$\frac{dN_{i,x}}{dx} = 0 \qquad (114)$$

$$\left(\mathrm{i = H+, CH3OH\ (M), H2O\ (W)}\right)$$

leads to:

$$N_{i,x} = N_{i,x=0} = N_{i,x=\delta_m} = const. \qquad (114a)$$

$N_{i,x=0}$, $N_{i,x=\delta_m}$ are the fluxes at the end of the membrane but on the "membrane phase side".

$$\therefore \quad N_{H^+,x} = \left(v_{H^+,x} c_{H^+}\right) =$$

$$c_{H^+}\, v_{H^+,x} = x_{H^+} c_T \left[\begin{array}{l} \left(\frac{M_{11}}{\det(L)}\right)\left(\left(c_T RT\right)\frac{dx_{H^+}}{dx} + z_{H^+} \mathrm{c_T F x_{H^+}} \frac{\mathrm{d\Phi}}{\mathrm{dx}}\right) + \\ \left(\frac{M_{12}}{\det(L)}\right)\left(\left(c_T RT\right)\frac{dx_M}{dx}\right) + \left(\frac{M_{13}}{\det(L)}\right)\left(\left(c_T RT\right)\frac{dx_W}{dx}\right) \end{array}\right] \qquad (115a)$$

$$N_{H^+,x} =$$

$$\left[\left(\frac{M_{11}}{\det(L)}\right)\left(\left(c_T^2 RT\right)x_{H^+}\frac{dx_{H^+}}{dx}\right) + \left(\frac{M_{12}}{\det(L)}\right)\left(\left(c_T^2 RT\right)x_{H^+}\frac{dx_M}{dx}\right) + \left(\frac{M_{13}}{\det(L)}\right)\left(\left(c_T^2 RT\right)x_{H^+}\frac{dx_W}{dx}\right)\right]$$

$$+ \left(\frac{M_{11}}{\det(L)}\right)\left(z_{H^+} F\, c_T^2\right)\left(x_{H^+}^2\right)\frac{\mathrm{d\Phi}}{\mathrm{dx}} \qquad (115b)$$

$$N_{M,x} = \left(v_{M,x} c_M\right) =$$

$$c_T\, x_M\, v_{M,x} = x_M c_T \left[\begin{array}{l} \left(\frac{M_{21}}{\det(L)}\right)\left(\left(c_T RT\right)\frac{dx_{H^+}}{dx} + z_{H^+} \mathrm{c_T F x_{H^+}} \frac{\mathrm{d\Phi}}{\mathrm{dx}}\right) + \\ \left(\frac{M_{22}}{\det(L)}\right)\left(\left(c_T RT\right)\frac{dx_M}{dx}\right) + \left(\frac{M_{23}}{\det(L)}\right)\left(\left(c_T RT\right)\frac{dx_W}{dx}\right) \end{array}\right] \qquad (116a)$$

$$N_{M,x} = \left(\frac{M_{21}}{\det(L)}\right)\left(c_T^2 RT\right)\left(x_M \frac{dx_{H^+}}{dx}\right) + \left(\frac{M_{22}}{\det(L)}\right)\left(c_T^2 RT\right)\left(x_M \frac{dx_M}{dx}\right) +$$

$$\left(\frac{M_{23}}{\det(L)}\right)\left(c_T^2 RT\right)\left(x_M \frac{dx_W}{dx}\right) + \left(\frac{M_{21}}{\det(L)}\right)\left(z_{H^+} F\, c_T^2\right)\left(x_M x_{H^+}\right)\frac{\mathrm{d\Phi}}{\mathrm{dx}}$$

(116b)

$$N_{W,x} = \left(v_{W,x} c_W\right) =$$

$$c_T\, x_W\, v_{W,x} = x_W c_T \left[\begin{array}{l} \left(\frac{M_{31}}{\det(L)}\right)\left(\left(c_T RT\right)\frac{dx_{H^+}}{dx} + z_{H^+} \mathrm{c_T F x_{H^+}} \frac{\mathrm{d}\Phi}{\mathrm{dx}}\right) + \\ \left(\frac{M_{32}}{\det(L)}\right)\left(\left(c_T RT\right)\frac{dx_M}{dx}\right) + \left(\frac{M_{33}}{\det(L)}\right)\left(\left(c_T RT\right)\frac{dx_W}{dx}\right) \end{array} \right] \qquad (117a)$$

$$N_{W,x} = \left(\frac{M_{31}}{\det(L)}\right)\left(c_T^2 RT\right)\left(x_W \frac{dx_{H^+}}{dx}\right) + \left(\frac{M_{32}}{\det(L)}\right)\left(c_T^2 RT\right)\left(x_W \frac{dx_M}{dx}\right) +$$

$$\left(\frac{M_{33}}{\det(L)}\right)\left(c_T^2 RT\right)\left(x_W \frac{dx_W}{dx}\right) + \left(\frac{M_{31}}{\det(L)}\right)\left(z_{H^+} F\, c_T^2\right)\left(x_W x_{H^+}\right)\frac{\mathrm{d}\Phi}{\mathrm{dx}} \qquad (117b)$$

Using Poisson equation, it was found for the membrane phase in 'Transport Set of Equations-I':

$$\left(\frac{d\Phi}{dx}\right) = \frac{-\left|\Phi^A - \Phi^C\right|}{\delta_m} + \left(\frac{z_{H^+}\bar{c}_{H^+} F}{2 \in}\right)\left(\delta_m - 2x\right) \qquad (118)$$

where; $\bar{c}_{H^+}$ = average concentration of H^+ with the entire membrane phase taken as the mixture of [mobile H^+ in the fluid phase], CH_3OH, H_2O and membrane material.

$= \bar{x}_{H^+} c_T$

δ_m = thickness of the membrane phase.

$$\therefore \left(\frac{d\Phi}{dx}\right) = \frac{-\left|\Phi^A - \Phi^C\right|}{\delta_m} + \left(\frac{z_{H^+}\bar{x}_{H^+} c_T F}{2 \in}\right)\left(\delta_m - 2x\right) \qquad (119)$$

Putting the above equation into Eqs. (115b), (116b), (117b):

$$N_{H^+,x} =$$

$$\left[\left(\frac{M_{11}}{\det(L)}\right)\left(\left(c_T^2 RT\right)\left[\frac{1}{2}\frac{dx_{H^+}^2}{dx}\right]\right) + \left(\frac{M_{12}}{\det(L)}\right)\left(\left(c_T^2 RT\right)x_{H^+}\frac{dx_M}{dx}\right) + \left(\frac{M_{13}}{\det(L)}\right)\left(\left(c_T^2 RT\right)x_{H^+}\frac{dx_W}{dx}\right)\right]$$

$$+ \left(\frac{M_{11}}{\det(L)}\right)\left(z_{H^+} F\, c_T^2\right) x_{H^+}^2 \left[\frac{-\left|\Phi^A - \Phi^C\right|}{\delta_m} + \left(\frac{z_{H^+}\bar{x}_{H^+} c_T F}{2 \in}\right)\left(\delta_m - 2x\right)\right] \qquad (120a)$$

$$N_{M,x} =$$

$$\left(\frac{M_{21}}{\det(L)}\right)\left(c_T^2 RT\right)\left(x_M \frac{dx_{H^+}}{dx}\right)+\left(\frac{M_{22}}{\det(L)}\right)\left(c_T^2 RT\right)\left(\frac{1}{2}\frac{dx_M^2}{dx}\right)+$$

$$\left(\frac{M_{23}}{\det(L)}\right)\left(c_T^2 RT\right)\left(x_M \frac{dx_W}{dx}\right)+$$

$$\left(\frac{M_{21}}{\det(L)}\right)\left(z_{H^+} F\, c_T^2\right)\left(x_M x_{H^+}\right)\left[\frac{-\left|\Phi^A-\Phi^C\right|}{\delta_m}+\left(\frac{z_{H^+}\bar{c}_{H^+}F}{2\in}\right)\left(\delta_m-2x\right)\right] \tag{120b}$$

$$N_{W,x} =$$

$$\left(\frac{M_{31}}{\det(L)}\right)\left(c_T^2 RT\right)\left(x_W \frac{dx_{H^+}}{dx}\right)+\left(\frac{M_{32}}{\det(L)}\right)\left(c_T^2 RT\right)\left(x_W \frac{dx_M}{dx}\right)+$$

$$\left(\frac{M_{33}}{\det(L)}\right)\left(c_T^2 RT\right)\left(\frac{1}{2}\frac{dx_W^2}{dx}\right)+$$

$$\left(\frac{M_{31}}{\det(L)}\right)\left(z_{H^+} F\, c_T^2\right)\left(x_W x_{H^+}\right)\left[\frac{-\left|\Phi^A-\Phi^C\right|}{\delta_m}+\left(\frac{z_{H^+}\bar{c}_{H^+}F}{2\in}\right)\left(\delta_m-2x\right)\right] \tag{120c}$$

The flux equations (120a), (120b), and (120c) are quite general in that they can be applied to a membrane made of any material, provided the information on the values of the interaction coefficients M_{ij} is available. The following equation for the voltage distribution in the membrane is from the solution of the Poisson equation for the "net charge" due to H^+ ions passing through the membrane in the company of H_2O molecules as well as CH_3OH if CH_3OH molecules are also permeating.

$$\left(\Phi-\Phi^A\right)=\left(\Phi^A-\Phi^C\right)\left(\frac{x}{\delta_m}\right)+\left(\frac{z_{H^+}\bar{c}_{H^+}F}{2\in}\right)\left(\delta_m x-x^2\right) \tag{121}$$

The expressions in Eqs. (120a), (120b), and (120c) indicate the fluxes of the species H^+, CH_3OH (M) and H_2O (W) via diffusion mechanism, where the diffusion flux of each

species is affected by the gradients of the concentrations of all mobile species, and via electric field effect.

Equations (120a) through (120c) are now transformed as follows:

For the treatment of Eq.(120a):

$$\left[x_{H^+} \frac{dx_M}{dx} \right] = \frac{d}{dx}\left(x_{H^+} x_M \right) - x_M \frac{dx_{H^+}}{dx}$$

$$\left[x_{H^+} \frac{dx_W}{dx} \right] = \frac{d}{dx}\left(x_{H^+} x_W \right) - x_W \frac{dx_{H^+}}{dx}$$

Using the above equations, Eq.(120a) is rewritten as:

$$N_{H^+,x} =$$

$$\left[\left(\frac{M_{11}}{\det(L)} \right) \left(\left(\frac{c_T^2 RT}{2} \right) \left[\frac{dx_{H^+}^2}{dx} \right] \right) + \left(\frac{M_{12}}{\det(L)} \right) \left(c_T^2 RT \right) \left(\frac{d}{dx}\left(x_{H^+} x_M \right) - x_M \frac{dx_{H^+}}{dx} \right) + \left(\frac{M_{13}}{\det(L)} \right) \left(c_T^2 RT \right) \left(\frac{d}{dx}\left(x_{H^+} x_W \right) - x_W \frac{dx_{H^+}}{dx} \right) \right] +$$

$$\left(\frac{M_{11}}{\det(L)} \right) \left(z_{H^+} F c_T^2 \right) x_{H^+}^2 \left[\frac{-\left| \Phi^A - \Phi^C \right|}{\delta_m} + \left(\frac{z_{H^+} \bar{c}_{H^+} F}{2 \in} \right) \left(\delta_m - 2x \right) \right] \qquad (121a)$$

For the treatment of Eq.(120b):

$$\left[x_M \frac{dx_{H^+}}{dx} \right] = \frac{d}{dx}\left(x_M x_{H^+} \right) - x_{H^+} \frac{dx_M}{dx}$$

$$\left[x_M \frac{dx_W}{dx} \right] = \frac{d}{dx}\left(x_M x_W \right) - x_W \frac{dx_M}{dx}$$

Using the above equations, Eq.(120b) is transformed into:

$$N_{M,x} = \left(\frac{M_{21}}{\det(L)} \right) \left(c_T^2 RT \right) \left(\frac{d}{dx}\left(x_M x_{H^+} \right) - x_{H^+} \frac{dx_M}{dx} \right) + \left(\frac{M_{22}}{\det(L)} \right) \left(\frac{c_T^2 RT}{2} \right) \left[\frac{dx_M^2}{dx} \right] +$$

$$\left(\frac{M_{23}}{\det(L)} \right) \left(c_T^2 RT \right) \left(\frac{d}{dx}\left(x_M x_W \right) - x_W \frac{dx_M}{dx} \right) +$$

$$\left(\frac{M_{21}}{\det(L)} \right) \left(z_{H^+} F c_T^2 \right) \left(x_M x_{H^+} \right) \left[\frac{-\left| \Phi^A - \Phi^C \right|}{\delta_m} + \left(\frac{z_{H^+} \bar{c}_{H^+} F}{2 \in} \right) \left(\delta_m - 2x \right) \right] \qquad (121b)$$

For the treatment of Eq.(120c):

$$\left[x_W \frac{dx_{H^+}}{dx} \right] = \frac{d}{dx}\left(x_W x_{H^+} \right) - x_{H^+} \frac{dx_W}{dx}$$

$$\left[x_W \frac{dx_M}{dx} \right] = \frac{d}{dx}\left(x_W x_M \right) - x_M \frac{dx_W}{dx}$$

Putting this information into Eq.(120c):

$$N_{W,x} =$$

$$\left(\frac{M_{31}}{\det(L)} \right) \left(c_T^2 RT \right) \left(\frac{d}{dx}\left(x_W x_{H^+} \right) - x_{H^+} \frac{dx_W}{dx} \right) +$$

$$\left(\frac{M_{32}}{\det(L)} \right) \left(c_T^2 RT \right) \left(\frac{d}{dx}\left(x_W x_M \right) - x_M \frac{dx_W}{dx} \right) +$$

$$\left(\frac{M_{33}}{\det(L)} \right) \left(\frac{c_T^2 RT}{2} \right) \left(\frac{dx_W^2}{dx} \right) +$$

$$\left(\frac{M_{31}}{\det(L)} \right) \left(z_{H^+} F c_T^2 \right) \left(x_W x_{H^+} \right) \left[\frac{-\left| \Phi^A - \Phi^C \right|}{\delta_m} + \left(\frac{z_{H^+} \bar{c}_{H^+} F}{2 \in} \right) \left(\delta_m - 2x \right) \right] \qquad (121c)$$

$$\bar{c}_{H^+} = \bar{x}_{H^+} c_T$$

where $\bar{x}_{H^+} = \dfrac{x_{H^+/@\,x=0} + x_{H^+/@\,x=\delta_M}}{2}$

Equations (121a), (121b), and (121c) describe the fluxes of the species H^+, CH_3OH (M) and H_2O (W) through the membrane via diffusion and electric field effect. Note the transport of CH_3OH (M) and H_2O (W), via electric field effect also, for these charge neutral species.

These equations are quite general. Also, for the condition of steady-state the fluxes $N_{H^+,x}$, $N_{M,x}$ and $N_{W,x}$ are invariant with respect to the distance x through the membrane phase.

In what follows an approximate method (i.e. engineering practice method) is followed to relate the fluxes to the species mole fractions. Here, diffusion interaction related parameters $\left(\frac{M}{\det(L)}\right)'s$ are assumed to be constant over the membrane phase thickness, δ_m. Total membrane phase molar concentration c_T is also taken constant. In fact, one may take the average values of these parameters at the membrane ends.

Treatment of Eq.(121a):

Multiply both sides of this Eq. By dx and integrate:

$$\int_{x=0}^{x=\delta_m} N_{H^+,x}\, dx =$$

$$\left(\overline{\frac{M_{11}}{\det(L)}}\right)\left(\frac{c_T^2 RT}{2}\right)\int_{x=0}^{x=\delta_m}\left(\frac{d\, x_{H^+}^2}{dx}\right)dx + \left(\overline{\frac{M_{12}}{\det(L)}}\right)\left(c_T^2 RT\right)\left\{\int_0^{\delta_m}\frac{d}{dx}\left(x_{H^+}x_M\right)dx - \int_{x=0}^{x=\delta_m}\left(x_M\frac{dx_{H^+}}{dx}\right)dx\right\}$$

$$+\left(\overline{\frac{M_{13}}{\det(L)}}\right)\left(c_T^2 RT\right)\left\{\int_0^{\delta_m}\frac{d}{dx}\left(x_{H^+}x_W\right)dx - \int_{x=0}^{x=\delta_m}\left(x_W\frac{dx_{H^+}}{dx}\right)dx\right\}$$

$$+\left(\overline{\frac{M_{11}}{\det(L)}}\right)\left(z_{H^+}Fc_T^2\right)\int_{x=0}^{x=\delta_m}\left\{x_{H^+}^2\left[\frac{-\left|\Phi^A-\Phi^C\right|}{\delta_m}+\left(\frac{z_{H^+}Fc_T\bar{x}_{H^+}}{2\in}\right)\left(\delta_m-2x\right)\right]\right\}dx \qquad (122a)$$

$$N_{H^+,x}\,\delta_m =$$

$$\left(\overline{\frac{M_{11}}{\det(L)}}\right)\left(\frac{c_T^2 RT}{2}\right)\left[x_{H^+}^2\Big|_{@\,x=\delta_m} - x_{H^+}^2\Big|_{@\,x=0}\right]$$

$$+\left(\overline{\frac{M_{12}}{\det(L)}}\right)\left(c_T^2 RT\right)\left\{\left(x_{H^+}x_M\right)\Big|_{@\,x=\delta_m} - \left(x_{H^+}x_M\right)\Big|_{@\,x=0} - \int_0^{\delta_m}\left(x_M\frac{dx_{H^+}}{dx}\right)dx\right\}$$

$$+\left(\overline{\frac{M_{13}}{\det(L)}}\right)\left(c_T^2 RT\right)\left\{\left(x_{H^+}x_W\right)\Big|_{@\,x=\delta_m} - \left(x_{H^+}x_W\right)\Big|_{@\,x=0} - \int_{x=0}^{x=\delta_m}\left(x_W\frac{dx_{H^+}}{dx}\right)dx\right\}$$

$$+\left(\overline{\frac{M_{11}}{\det(L)}}\right)\left(z_{H^+}Fc_T^2\right)\int_0^{\delta_m}\left\{x_{H^+}^2\left[\frac{-\left|\Phi^A-\Phi^C\right|}{\delta_m}+\left(\frac{z_{H^+}Fc_T\bar{x}_{H^+}}{2\in}\right)\left(\delta_m-2x\right)\right]\right\}dx \qquad (122b)$$

Now, some approximations have to be made

$$\int_0^{\delta_m}\left(x_M\frac{dx_{H^+}}{dx}\right)dx \cong \bar{x}_M \int_{x=0}^{x=\delta_m}\left(\frac{dx_{H^+}}{dx}\right)dx$$

$$= \bar{x}_M\left[x_{H^+}\Big|_{@\,x=\delta_M} - x_{H^+}\Big|_{@\,x=0}\right] \tag{122c}$$

$$\text{where } \bar{x}_M = \left(\frac{\int_0^{\delta_m} x_M\,dx}{\delta_M}\right) = \left(\frac{\left(x_M\right)\Big|_{@\,x=0} - \left(x_M\right)\Big|_{@\,x=\delta_m}}{2}\right) \tag{122d}$$

$$\int_0^{\delta_m}\left(x_W\frac{dx_{H^+}}{dx}\right)dx \cong \bar{x}_W \int_{x=0}^{x=\delta_m}\left(\frac{dx_{H^+}}{dx}\right)dx$$

$$= \bar{x}_W\left[x_{H^+}\Big|_{@\,x=\delta_M} - x_{H^+}\Big|_{@\,x=0}\right] \tag{122e}$$

$$\text{where } \bar{x}_M = \left(\frac{\int_0^{\delta_m} x_W\,dx}{\delta_m}\right) = \left(\frac{\left(x_W\right)\Big|_{@\,x=0} - \left(x_W\right)\Big|_{@\,x=\delta_m}}{2}\right)$$

$$\int_0^{\delta_m}\left\{x_{H^+}^2\left[\frac{-\left|\Phi^A - \Phi^C\right|}{\delta_m} + \left(\frac{z_{H^+}Fc_T\bar{x}_{H^+}}{2\in}\right)\left(\delta_m - 2x\right)\right]\right\}dx \cong$$

$$\left(\bar{x}_{H^+}^2\right)\int_0^{\delta_m}\left\{\left[\frac{-\left|\Phi^A - \Phi^C\right|}{\delta_m} + \left(\frac{z_{H^+}Fc_T\bar{x}_{H^+}}{2\in}\right)\left(\delta_m - 2x\right)\right]\right\}dx\,, \tag{122f}$$

$$\text{where } \left(\overline{x_{H^+}^2}\right) = \left(\frac{\int_0^{\delta_m}\left(x_{H^+}^2\right)dx}{\delta_m}\right) \tag{122g}$$

$$= \left(\frac{\left(x_{H^+}^2\right)\Big|_{@\,x=0} - \left(x_{H^+}^2\right)\Big|_{@\,x=\delta_M}}{2}\right) \tag{122h}$$

Equation (122f) becomes

$$\int_0^{\delta_m}\left\{x_{H^+}^2\left[\frac{-\left|\Phi^A-\Phi^C\right|}{\delta_m}+\left(\frac{z_{H^+}Fc_T\bar{x}_{H^+}}{2\in}\right)(\delta_m-2x)\right]\right\}dx =$$

$$\left(\bar{x}_{H^+}^2\right)\left[-\left|\Phi^A-\Phi^C\right|+\left(\frac{z_{H^+}Fc_T\bar{x}_{H^+}}{2\in}\right)\left(\delta_m^2-\frac{2\delta_m^2}{2}\right)\right] = \left(\bar{x}_{H^+}^2\right)\left[-\left|\Phi^A-\Phi^C\right|\right] \qquad (122i)$$

Equation (122b), now, becomes

$$N_{H^+,x}\,\delta_m =$$

$$\left(\overline{\frac{M_{11}}{\det(L)}}\right)\left(\frac{c_T^2RT}{2}\right)\left[x_{H^+}^2\Big|_{@\,x=\delta_m}-x_{H^+}^2\Big|_{@\,x=0}\right]$$

$$+\left(\overline{\frac{M_{12}}{\det(L)}}\right)\left(c_T^2RT\right)\left\{\left(x_{H^+}x_M\right)\Big|_{@\,x=\delta_m}-\left(x_{H^+}x_M\right)\Big|_{@\,x=0}-\bar{x}_M\left(x_{H^+}\Big|_{@\,x=\delta_m}-x_{H^+}\Big|_{@\,x=0}\right)\right\}$$

$$+\left(\overline{\frac{M_{13}}{\det(L)}}\right)\left(c_T^2RT\right)\left\{\left(x_{H^+}x_W\right)\Big|_{@\,x=\delta_m}-\left(x_{H^+}x_W\right)\Big|_{@\,x=0}-\bar{x}_W\left(x_{H^+}\Big|_{@\,x=\delta_m}-x_{H^+}\Big|_{@\,x=0}\right)\right\}$$

$$+\left(\overline{\frac{M_{11}}{\det(L)}}\right)\left(z_{H^+}Fc_T^2\right)\left[-\left|\Phi^A-\Phi^C\right|\right]\left(\bar{x}_{H^+}^2\right)$$

$$N_{H^+,x} =$$

$$\left(\overline{\frac{M_{11}}{\det(L)}}\right)\left(\frac{c_T^2RT}{2}\right)\left(\frac{x_{H^+}^2\Big|_{@\,x=\delta_m}-x_{H^+}^2\Big|_{@\,x=0}}{\delta_m}\right) \qquad \text{Term(1)}$$

$$+\left(\overline{\frac{M_{12}}{\det(L)}}\right)\left(c_T^2RT\right)\left\{\frac{\left(x_{H^+}x_M\right)\Big|_{@\,x=\delta_m}-\left(x_{H^+}x_M\right)\Big|_{@\,x=0}}{\delta_m}-\bar{x}_M\left(\frac{x_{H^+}\Big|_{@\,x=\delta_m}-x_{H^+}\Big|_{@\,x=0}}{\delta_m}\right)\right\}$$

Term (2)

$$+\left(\overline{\frac{M_{13}}{\det(L)}}\right)\left(c_T^2RT\right)\left\{\frac{\left(x_{H^+}x_W\right)\Big|_{@\,x=\delta_m}-\left(x_{H^+}x_W\right)\Big|_{@\,x=0}}{\delta_m}-\bar{x}_W\left(\frac{x_{H^+}\Big|_{@\,x=\delta_m}-x_{H^+}\Big|_{@\,x=0}}{\delta_m}\right)\right\}$$

Term (3)

$$+\left(\overline{\frac{M_{11}}{\det(L)}}\right)\left(z_{H^+}Fc_T^2\right)\left[\frac{-\left|\Phi^A-\Phi^C\right|}{\delta_m}\right]\left(\bar{x}_{H^+}^2\right) \qquad \text{Term (4)}$$

(123)

Check: Units :

$$\left(\overline{\frac{M_{ij}}{\det(L)}}\right) = \left[\frac{\left(\frac{J.s}{m^5}\right)^2}{\left(\frac{J.s}{m^5}\right)^3}\right] = \left[\frac{m^5}{J.s}\right] = \left[\frac{m^5}{J.s}\right]$$

$$\left(c_T^2 RT\right) = \left[\left(\frac{mol}{m^3}\right)^2 . \left(\frac{J}{mol}\right)\right] = \left(\frac{mol}{m^6}.J\right)$$

$$\left[\frac{1}{\delta_m}\right] = \left[\frac{1}{m}\right]$$

Units of each of the terms : (1), (2), (3):

$$\left[\frac{m^5}{J.s}\right]\left(\frac{mol}{m^6}.J\right)\left[\frac{1}{m}\right] = \left(\frac{mol}{m^2 - s}\right)$$

Term (4) :

$$\left[\frac{m^5}{J.s}\right].\left(\frac{coulomb}{mol}\right)\left(\frac{mol}{m^3}\right)^2\left[\frac{volt}{m}\right] = \left(\frac{mol}{J.s - m^2}\right)[\mathrm{J}] = \left(\frac{mol}{m^2 - s}\right)$$

Equation (123) is dimensionally correct.

Treatment of Eq.(121b):

Multiply this Eq. by dx and integrate over the membrane:

$$N_{M,x}\,\delta_m =$$

$$\left(\overline{\frac{M_{21}}{\det(L)}}\right)\left(c_T^2 RT\right)\left\{\left(x_M x_{H^+}\right)\Big|_{@\,x=\delta_m} - \left(x_M x_{H^+}\right)\Big|_{@\,x=0} - \bar{x}_{H^+}\left(x_M\Big|_{@\,x=\delta_m} - x_M\Big|_{@\,x=0}\right)\right\}$$

$$+\left(\overline{\frac{M_{22}}{\det(L)}}\right)\left(\frac{c_T^2 RT}{2}\right)\left[x_M^2\Big|_{@\,x=\delta_m} - x_M^2\Big|_{@\,x=0}\right]$$

$$+\left(\overline{\frac{M_{23}}{\det(L)}}\right)\left(c_T^2 RT\right)\left\{\left(x_M x_W\right)\Big|_{@\,x=\delta_m} - \left(x_M x_W\right)\Big|_{@\,x=0} - \bar{x}_W\left(x_M\Big|_{@\,x=\delta_m} - x_M\Big|_{@\,x=0}\right)\right\}$$

$$+\left(\overline{\frac{M_{21}}{\det(L)}}\right)\left(z_{H^+} F c_T^2\right)\left[-\left|\Phi^A - \Phi^C\right|\right]\left(\overline{x_M x_{H^+}}\right)$$

(124)

Divide both sides by δ_m :

$$N_{M,x} =$$

$$\left(\overline{\frac{M_{21}}{\det(L)}}\right)\left(c_T^2 RT\right)\left\{\frac{\left(x_M x_{H^+}\right)\Big|_{@\,x=\delta_m} - \left(x_M x_{H^+}\right)\Big|_{@\,x=0}}{\delta_m} - \bar{x}_{H^+}\left(\frac{x_M\Big|_{@\,x=\delta_m} - x_M\Big|_{@\,x=0}}{\delta_m}\right)\right\}$$

$$+\left(\overline{\frac{M_{22}}{\det(L)}}\right)\left(\frac{c_T^2 RT}{2}\right)\left(\frac{x_M^2\Big|_{@\,x=\delta_m} - x_M^2\Big|_{@\,x=0}}{\delta_m}\right)$$

$$+\left(\overline{\frac{M_{23}}{\det(L)}}\right)\left(c_T^2 RT\right)\left\{\frac{\left(x_M x_W\right)\Big|_{@\,x=\delta_m} - \left(x_M x_W\right)\Big|_{@\,x=0}}{\delta_m} - \bar{x}_W\left(\frac{x_M\Big|_{@\,x=\delta_m} - x_M\Big|_{@\,x=0}}{\delta_m}\right)\right\}$$

$$+\left(\overline{\frac{M_{21}}{\det(L)}}\right)\left(\overline{x_M x_{H^+}}\right)\left(z_{H^+} F c_T^2\right)\left[\frac{-\left|\Phi^A - \Phi^C\right|}{\delta_m}\right] \qquad (125)$$

Treatment of Eq.(121c):

Multiply (121c) by dx and integrate term by term over the membrane for x = 0 $\rightarrow$ x = δ_m:

$$N_{W,x}\,\delta_m =$$

$$\left(\overline{\frac{M_{31}}{\det(L)}}\right)\left(c_T^2 RT\right)\left\{\left(x_W x_{H^+}\right)\Big|_{@\,x=\delta_m} - \left(x_W x_{H^+}\right)\Big|_{@\,x=0} - \bar{x}_{H^+}\left(x_W\Big|_{@\,x=\delta_m} - x_W\Big|_{@\,x=0}\right)\right\}$$

$$+\left(\overline{\frac{M_{32}}{\det(L)}}\right)\left(c_T^2 RT\right)\left\{\left(x_W x_M\right)\Big|_{@\,x=\delta_m} - \left(x_W x_M\right)\Big|_{@\,x=0} - \bar{x}_W\left(x_W\Big|_{@\,x=\delta_m} - x_W\Big|_{@\,x=0}\right)\right\}$$

$$+\left(\overline{\frac{M_{33}}{\det(L)}}\right)\left(\frac{c_T^2 RT}{2}\right)\left[x_W^2\Big|_{@\,x=\delta_m} - x_W^2\Big|_{@\,x=0}\right]$$

$$+\left(\overline{\frac{M_{31}}{\det(L)}}\right)\left(z_{H^+} F c_T^2\right)\left[-\left|\Phi^A - \Phi^C\right|\right]\left(\overline{x_W x_{H^+}}\right) \qquad (126)$$

$$N_{W,x} =$$

$$\left(\overline{\frac{M_{31}}{\det(L)}}\right)\left(c_T^2 RT\right)\left\{\frac{\left(x_W x_{H^+}\right)\Big|_{@\,x=\delta_m} - \left(x_W x_{H^+}\right)\Big|_{@\,x=0}}{\delta_m} - \bar{x}_{H^+}\left(\frac{x_W\Big|_{@\,x=\delta_m} - x_W\Big|_{@\,x=0}}{\delta_m}\right)\right\}$$

$$+\left(\frac{\overline{M_{32}}}{\det(L)}\right)\left(c_T^2 RT\right)\left\{\frac{\left(x_W x_M\right)\Big|_{@\,x=\delta_m}-\left(x_W x_M\right)\Big|_{@\,x=0}}{\delta_m}-\bar{x}_M\left(\frac{x_W\Big|_{@\,x=\delta_m}-x_W\Big|_{@\,x=0}}{\delta_m}\right)\right\}$$

$$+\left(\frac{\overline{M_{33}}}{\det(L)}\right)\left(\frac{c_T^2 RT}{2}\right)\left(\frac{x_W^2\Big|_{@\,x=\delta_m}-x_W^2\Big|_{@\,x=0}}{\delta_m}\right)$$

$$+\left(\frac{\overline{M_{31}}}{\det(L)}\right)\left(z_{H^+}Fc_T^2\right)\left(\overline{x_W x_{H^+}}\right)\left[\frac{-\left|\Phi^A-\Phi^C\right|}{\delta_m}\right] \qquad (127)$$

Comment:

In Eqs. (123), (125), and (127), on the right-hand side of each equations, the terms contribute to the flux of the concerned species via the multi component diffusion and the last term on the right-hand side represents the flux due to electric field. In the case of M (CH_3OH) and W (H_2O), the last term is defined here as the electro-osmotic flux.

Equations (123), (125) and (127) are now written in terms of concentrations rather than in terms of mole fractions:

$$N_{H^+,x}=$$

$$\left(\frac{\overline{M_{11}}}{\det(L)}\right)\left(\frac{RT}{2}\right)\left(\frac{\left(c_{H^+}\Big|_{@\,x=\delta_m}\right)^2-\left(c_{H^+}\Big|_{@\,x=0}\right)^2}{\delta_m}\right)$$

$$+\left(\frac{\overline{M_{12}}}{\det(L)}\right)(RT)\left\{\frac{\left(c_{H^+}c_M\right)\Big|_{@\,x=\delta_m}-\left(c_{H^+}c_M\right)\Big|_{@\,x=0}}{\delta_m}-\bar{c}_M\left(\frac{c_{H^+}\Big|_{@\,x=\delta_m}-c_{H^+}\Big|_{@\,x=0}}{\delta_m}\right)\right\}$$

$$+\left(\frac{\overline{M_{13}}}{\det(L)}\right)(RT)\left\{\frac{\left(c_{H^+}c_W\right)\Big|_{@\,x=\delta_m}-\left(c_{H^+}c_W\right)\Big|_{@\,x=0}}{\delta_m}-\bar{c}_W\left(\frac{c_{H^+}\Big|_{@\,x=\delta_m}-c_{H^+}\Big|_{@\,x=0}}{\delta_m}\right)\right\}$$

$$+\left(\frac{\overline{M_{11}}}{\det(L)}\right)\left(z_{H^+}F\right)\left[\frac{-\left|\Phi^A-\Phi^C\right|}{\delta_m}\right]\left(\bar{c}_{H^+}^2\right) \qquad (128)$$

$$N_{M,x}=$$

$$\left(\overline{\frac{M_{21}}{\det(L)}}\right)(RT)\left\{\frac{\left(c_M c_{H^+}\right)\Big|_{@\,x=\delta_m}-\left(c_M c_{H^+}\right)\Big|_{@\,x=0}}{\delta_m}-\bar{c}_{H^+}\left(\frac{c_M\Big|_{@\,x=\delta_m}-c_M\Big|_{@\,x=0}}{\delta_m}\right)\right\}$$

$$+\left(\overline{\frac{M_{22}}{\det(L)}}\right)\left(\frac{RT}{2}\right)\left(\frac{\left(c_M\Big|_{@\,x=\delta_m}\right)^2-\left(c_M\Big|_{@\,x=0}\right)^2}{\delta_m}\right)$$

$$+\left(\overline{\frac{M_{23}}{\det(L)}}\right)(RT)\left\{\frac{\left(c_M c_W\right)\Big|_{@\,x=\delta_m}-\left(c_M c_W\right)\Big|_{@\,x=0}}{\delta_m}-\bar{c}_W\left(\frac{c_M\Big|_{@\,x=\delta_m}-c_M\Big|_{@\,x=0}}{\delta_m}\right)\right\}$$

$$+\left(\overline{\frac{M_{21}}{\det(L)}}\right)\left(\overline{c_M c_{H^+}}\right)\left(z_{H^+}F\right)\left[\frac{-\left|\Phi^A-\Phi^C\right|}{\delta_m}\right] \qquad (129)$$

$$N_{W,x}=$$

$$\left(\overline{\frac{M_{31}}{\det(L)}}\right)(RT)\left\{\frac{\left(c_W c_{H^+}\right)\Big|_{@\,x=\delta_m}-\left(c_W c_{H^+}\right)\Big|_{@\,x=0}}{\delta_m}-\bar{c}_{H^+}\left(\frac{c_W\Big|_{@\,x=\delta_m}-c_W\Big|_{@\,x=0}}{\delta_m}\right)\right\}$$

$$+\left(\overline{\frac{M_{32}}{\det(L)}}\right)(RT)\left\{\frac{\left(c_W c_M\right)\Big|_{@\,x=\delta_m}-\left(c_W c_M\right)\Big|_{@\,x=0}}{\delta_m}-\bar{c}_M\left(\frac{c_W\Big|_{@\,x=\delta_m}-c_W\Big|_{@\,x=0}}{\delta_m}\right)\right\}$$

$$+\left(\overline{\frac{M_{33}}{\det(L)}}\right)\left(\frac{RT}{2}\right)\left(\frac{c_W^2\Big|_{@\,x=\delta_m}-c_W^2\Big|_{@\,x=0}}{\delta_m}\right)$$

$$+\left(\overline{\frac{M_{31}}{\det(L)}}\right)\left(z_{H^+}F\right)\left(\overline{c_W c_{H^+}}\right)\left[\frac{-\left|\Phi^A-\Phi^C\right|}{\delta_m}\right] \qquad (130)$$

Now, the species H^+, CH_3OH (M), and H_2O (W) concentrations in the membrane phase at its boundaries with the electrodes are expressed in terms of the species compositions in the porous electrodes using the concept of phase equilibria between the membrane and electrodes with regard to each species.

For the liquid mixture in the porous anode in equilibrium with the membrane phase at x = 0, with regard to a species i, the condition for equilibrium is

$$\mu_i^{A-e} = \mu_i^{m-eo} \tag{131}$$

(i = CH_3OH, H_2O)

$$\mu_i^{A-e} = \mu_i^{oL} + \text{RT } \ln\left(\gamma_i^{L-A} x_i^{L-A-e}\right) \tag{132}$$

$$\mu_i^{m-eo} = \mu_i^{om} + \text{RT } \ln\left(\gamma_i^{c,m-A} \frac{c_i^{m-eo}}{c_o}\right) \tag{133}$$

(i = CH_3OH, H_2O)

where μ_i^{oL} = chemical potential of the pure liquid species i at the temperature and pressure of the mixture in the anode,

μ_i^{om} = chemical potential of the pure liquid species i at the temperature and pressure of the mixture in the membrane phase,

x_i^{L-A-e} = mole fraction of species i in the liquid phase mixture in the porous anode end in contact with the membrane,

c_i^{m-eo} = mole concentration of species i [mol per unit volume] in the membrane phase in contact with the porous anode end at x = 0,

c_o = 1 mol per unit volume; used here as adjusting parameter to make $\left(\frac{c_i^{M-eo}}{c_o}\right)$ a dimensionless quantity,

γ_i^{L-A} = activity coefficient of species i in the liquid phase mixture in the porous anode to account for the nonideal behavior of species i in the mixture,

$\gamma_i^{c,m-A}$ = activity coefficient of species i in the membrane phase to account for the nonideal behavior.

The standard state chemical potentials for the liquid phase in the anode, μ_i^{oL}, and for the membrane phase, μ_i^{om}, are assumed to be identical, i.e. $\mu_i^{oL} = \mu_i^{om}$,

Eqs. (131), (132),and (133) lead to

$$\gamma_i^{c,m-A} \frac{c_i^{m-eo}}{c_o} = \gamma_i^{L-A} x_i^{L-A-e} \tag{134}$$

This leads to:

$$c_i^{m-eo} = \left[\frac{\gamma_i^{L-A}}{\gamma_i^{c,m-A}}\right] x_i^{L-A-e}\, c_o \qquad (135)$$

$$= s_i^{L-A-m}\, x_i^{L-A-e}\, c_o \qquad (136)$$

(i = CH_3OH, H_2O)

Here, $s_i^{L-A-m} = \left[\frac{\gamma_i^{L-A}}{\gamma_i^{c,m-A}}\right]$, has been defined as the liquid solubility coefficient of component i in the membrane phase corresponding to the liquid phase composition in the anode. Note that c_i^{m-eo} is the molar concentration of the species i in the membrane phase at x = 0.

Following the similar procedure, it leads to

$$c_i^{m-e} = s_i^{L-C-m}\, x_i^{L-C-e}\, c_o \qquad (137)$$

(i = CH_3OH, H_2O)

where c_i^{m-e} = molar concentration of species i in the membrane phase at x = δ_m,

$s_i^{L-C-m} = \left[\frac{\gamma_i^{L-C}}{\gamma_i^{c,m-C}}\right]$, the liquid solubility coefficient of component i in the membrane phase corresponding to the mixture composition in the porous cathode end in contact with the membrane at x = δ_m.

If the dependence of the solubility coefficient of a species i in the membrane phase on compositon can be relaxed; then, one may set

$s_i^{L-A-m} = s_i^{L-C-m} = s_i^m$ (solubility coefficient of the species i in the membrane phase) (138)

Equations (136) and (137) are rewritten as

$$c_i^{m-eo} = s_i^m\, x_i^{L-A-e}\, c_o \qquad (139a)$$

(at the membrane-anode interface)

and $$c_i^{m-e} = s_i^m\, x_i^{L-C-e}\, c_o \qquad (139b)$$

(at the membrane-cathode interface)

(i = CH_3OH, H_2O)

where s_i^m = solubility coefficient of the species i in the membrane phase at the prevailing temperature and pressure conditions.

Treatment of H^+:

$$\mu_{H^+}^{A-e} = \mu_{H^+}^{m,eo} \tag{140}$$

where $\mu_{H^+}^{A-e}$ = electrochemical potential of H^+ in the porous anode end in contact with the membrane phase,

$\mu_{H^+}^{m,eo}$ = electrochemical potential of H^+ in the membrane phase end in contact with the anode at x = 0.

The electrochemical potential of H^+ is expressed as

$$\mu_{H^+} = \mathrm{RT}\ \ln\left(\lambda_{H^+}^{\theta} m_{H^+} \gamma_{H^+}\right) \tag{141}$$

where m_{H^+} = molality of H^+ in the solution in a porous electrode or in the membrane phase,

$\gamma_{H^+} = \gamma_{H^+}$ (temperature, pressure and compositon) = activity coefficient of H^+,

$\lambda_{H^+}^{\theta}$ = a proportionality constant, independent of composition and electrical state, but characteristic of H^+ and the solvent and dependent on temperature and pressure.

Equation (141) is used in Eq.(140) to obtain

$$\lambda_{H^+}^{\theta,A}\ m_{H^+}^{A-e}\ \gamma_{H^+}^{A-e} = \lambda_{H^+}^{\theta,m}\ m_{H^+}^{m-eo}\ \gamma_{H^+}^{m,eo} \tag{142}$$

If it can be allowed that $\lambda_{H^+}^{\theta,A} = \lambda_{H^+}^{\theta,M}$ (it may become possible if one can assume that water is solvent for the mobile H^+ ions in the porous anode and membrane); then, Eq.(142) becomes

$$m_{H^+}^{A-e}\ \gamma_{H^+}^{A-e} = m_{H^+}^{m-eo}\ \gamma_{H^+}^{m,eo} \tag{143}$$

$$m_{H^+}^{m-eo} = m_{H^+}^{A-e}\left(\frac{\gamma_{H^+}^{A-e}}{\gamma_{H^+}^{m,eo}}\right) \tag{143a}$$

$$\frac{c_{H^+}^{m-eo}}{\left(c_W^{m-eo} M_W\right)} = \frac{c_{H^+}^{A-e}}{\left(c_W^{A-e} M_W\right)}\left(\frac{\gamma_{H^+}^{A-e}}{\gamma_{H^+}^{m,eo}}\right)$$

$$c_{H^+}^{m-eo} = \left[\left(\frac{c_W^{m-eo}}{c_W^{A-e}}\right)\left(\frac{\gamma_{H^+}^{A-e}}{\gamma_{H^+}^{m,eo}}\right)\right] c_{H^+}^{A-e} \qquad (143b)$$

The solubility coefficient of H^+ ions in the membrane phase in the presence of water may be defined as

$$s_{H^+}^{L-m-A} = \left[\left(\frac{c_W^{M-eo}}{c_W^{A-e}}\right)\left(\frac{\gamma_{H^+}^{A-e}}{\gamma_{H^+}^{m,eo}}\right)\right] \qquad (144)$$

where c_W^{m-eo} = molar concentration of water in the membrane phase end in contact with the porous anode at x = 0,

c_W^{A-e} = molar concentration of water in the porous anode end in contact with the water,

$\gamma_{H^+}^{A-e}$, $\gamma_{H^+}^{m,eo}$ = activity coefficients of H^+ ion in the porous anode solution and in the membrane phase solution, respectively, at the membrane-anode interface at x = 0.

Note that $s_{H^+}^{L-m-A}$ is controlled by the product of $\left(\frac{c_W^{m-eo}}{c_W^{A-e}}\right)$ and $\left(\frac{\gamma_{H^+}^{A-e}}{\gamma_{H^+}^{m,eo}}\right)$.

It can be assumed that $\left(\frac{\gamma_{H^+}^{A-e}}{\gamma_{H^+}^{m,eo}}\right) \cong 1$

Then, $s_{H^+}^{L-m-A} \cong \left(\frac{c_W^{m-eo}}{c_W^{A-e}}\right)$.

From Eqs. (143b) and (144),

$$c_{H^+}^{m-eo} = s_{H^+}^{L-m-A}\, c_{H^+}^{A-e} \qquad (145)$$

Following the similar procedure it can be shown that

$$c_{H^+}^{m-e} = s_{H^+}^{L-m-C}\, c_{H^+}^{C-e} \qquad (146)$$

where $c_{H^+}^{m-e}$ = molar concentration of H^+ in the membrane phase end in contact with the porous cathode at $x = \delta_m$,

$c_{H^+}^{C-e}$ = molar concentration of H^+ ion in the mixture in the porous cathode end in contact with the membrane at $x = \delta_m$,

$s_{H^+}^{L-m-C} = \left[\left(\frac{c_W^{m-e}}{c_W^{C-e}}\right)\left(\frac{\gamma_{H^+}^{C-e}}{\gamma_{H^+}^{m,e}}\right)\right]$ defined as the solubility coefficient of H^+ ions in the membrane phase end in contact with the porous cathode at x = δ_m,

$\left(\frac{c_W^{m-e}}{c_W^{C-e}}\right)$ = ratio of molar concentration of water in the membrane to the molar concentration of water in the porous cathode phase end at the membrane-cathode interface at x = δ_m,

$\left(\frac{\gamma_{H^+}^{C-e}}{\gamma_{H^+}^{m,e}}\right)$ = ratio of H^+ ion activity coefficient in the porous cathode to that in the membrane phase at the cathode-membrane interface.

If it can be allowed that

$$s_{H^+}^{L-m-A} = s_{H^+}^{L-m-C} = s_{H^+}^{m};$$

then, Eqs. (145) and (146) are written as

$$c_{H^+}^{m-eo} = s_{H^+}^{m}\, c_{H^+}^{A-e} \tag{147}$$

$$c_{H^+}^{m-e} = s_{H^+}^{m}\, c_{H^+}^{C-e} \tag{148}$$

Molar concentrations of H^+, CH_3OH (M), and H_2O (W) appearing in the membrane phase in Eqs. (128), (129), and (130) are expressed in terms of the concentrations of the species in the porous anode and cathode using Eqs. (139a), (139b), (147) and (148) to obtain

$$N_{H^+,x} =$$

$$\left(s_{H^+}^{m}\right)^2\left(\frac{\overline{M_{11}}}{\det(L)}\right)\left(\frac{RT}{2}\right)\left(\frac{\left(c_{H^+}^{C-e}\right)^2-\left(c_{H^+}^{A-e}\right)^2}{\delta_m}\right)$$

$$+\left(s_{H^+}^{m}\, s_M^{m}\right)\left(\frac{\overline{M_{12}}}{\det(L)}\right)(RT)$$

$$\left[\left[\frac{c_{H^+}^{C-e}\left(x_M^{C-e}c_o\right)-c_{H^+}^{A-e}\left(x_M^{A-e}c_o\right)}{\delta_m}\right]-\left[\left(\frac{x_M^{A-e}+x_M^{C-e}}{2}\right)c_o\right]\left[\frac{c_{H^+}^{C-e}-c_{H^+}^{A-e}}{\delta_m}\right]\right]$$

$$+\left(s_{H^+}^m s_W^m\right)\left(\frac{\overline{M_{13}}}{\det(L)}\right)(RT)$$

$$\left[\left[\frac{c_{H^+}^{C-e}\left(x_W^{C-e}c_o\right)-c_{H^+}^{A-e}\left(x_W^{A-e}c_o\right)}{\delta_m}\right]-\left[\left(\frac{x_W^{C-e}+x_W^{A-e}}{2}\right)c_o\right]\left[\frac{c_{H^+}^{C-e}-c_{H^+}^{A-e}}{\delta_m}\right]\right]$$

$$+\left(s_{H^+}^m\right)^2\left(\frac{\overline{M_{11}}}{\det(L)}\right)\left(z_{H^+}F\right)\left(\frac{\left(c_{H^+}^{A-e}\right)^2+\left(c_{H^+}^{C-e}\right)^2}{2}\right)\left[\frac{-\left|\Phi^A-\Phi^C\right|}{\delta_m}\right] \quad (149)$$

$$N_{M,x}=$$

$$\left(s_{H^+}^m s_M^m\right)\left(\frac{\overline{M_{21}}}{\det(L)}\right)(RT)\left[\left[\frac{\left(c_{H^+}^{C-e}x_M^{C-e}-c_{H^+}^{A-e}x_M^{A-e}\right)c_o}{\delta_m}\right]-\left[\left[\frac{c_{H^+}^{C-e}+c_{H^+}^{A-e}}{2}\right]\left(\frac{x_M^{C-e}-x_M^{A-e}}{\delta_m}\right)c_o\right]\right]$$

$$+\left(s_M^m\right)^2\left(\frac{\overline{M_{22}}}{\det(L)}\right)\left(\frac{RT}{2}\right)\left(\frac{\left[\left(\left(x_M^{C-e}\right)^2-\left(x_M^{A-e}\right)^2\right)c_o^2\right]}{\delta_m}\right)$$

$$+\left(s_M^m s_W^m\right)\left(\frac{\overline{M_{23}}}{\det(L)}\right)(RT)\left[\frac{\left(x_M^{C-e}x_W^{C-e}-x_M^{A-e}x_W^{A-e}\right)c_o^2}{\delta_m}-\left(\frac{x_W^{C-e}+x_W^{A-e}}{2}\right)\left(\frac{x_M^{C-e}-x_M^{A-e}}{\delta_m}\right)c_o^2\right]$$

$$+\left(s_M^m s_{H^+}^m\right)\left(\frac{\overline{M_{21}}}{\det(L)}\right)\left(z_{H^+}F\right)\left[\frac{\left[\left(x_M^{C-e}c_{H^+}^{C-e}+x_M^{A-e}c_{H^+}^{A-e}\right)c_o\right]}{2}\right]\left[\frac{-\left|\Phi^A-\Phi^C\right|}{\delta_m}\right] \quad (150)$$

$$N_{W,x}=$$

$$\left(s_{H^+}^m s_W^m\right)\left(\frac{\overline{M_{31}}}{\det(L)}\right)(RT)\left[\left[\frac{\left(c_{H^+}^{C-e}x_W^{C-e}-c_{H^+}^{A-e}x_W^{A-e}\right)c_o}{\delta_m}\right]-\left[\left[\frac{c_{H^+}^{C-e}+c_{H^+}^{A-e}}{2}\right]\left(\frac{x_W^{C-e}-x_W^{A-e}}{\delta_m}\right)c_o\right]\right]$$

$$+\left(s_W^m s_M^m\right)\left(\frac{\overline{M_{32}}}{\det(L)}\right)(RT)\left[\frac{\left(x_W^{C-e}x_M^{C-e}-x_W^{A-e}x_M^{A-e}\right)c_o^2}{\delta_m}-\left(\frac{x_M^{C-e}+x_M^{A-e}}{2}\right)\left(\frac{x_W^{C-e}-x_W^{A-e}}{\delta_m}\right)c_o^2\right]$$

$$+\left(s_W^m\right)^2\left(\frac{\overline{M_{33}}}{\det(L)}\right)\left(\frac{RT}{2}\right)\left(\frac{\left[\left(\left(x_W^{C-e}\right)^2-\left(x_W^{A-e}\right)^2\right)c_o^2\right]}{\delta_m}\right)$$

$$+\left(s_W^m s_{H^+}^m\right)\left(\frac{\overline{M_{31}}}{\det(L)}\right)\left(z_{H^+}F\right)\left[\frac{\left[\left(x_W^{C-e}c_{H^+}^{C-e}+x_W^{A-e}c_{H^+}^{A-e}\right)c_o\right]}{2}\right]\left[\frac{-\left|\Phi^A-\Phi^C\right|}{\delta_m}\right] \quad (151)$$

5 Conclusions

Derivation of the transport flux equations for a direct methanol fuel cell solid polymer electrolyte membrane using i) moderately dilute solution theory based on Fickian diffusion, ii) concentrated solution theory based on the generalized Stefan-Maxwell equations, and iii) concentrated solution theory based on the Onsager irreversible thermodynamics approach to transport processes have been presented. The developed equations account for the effect of the voltage, pressure and the species concentration gradients on their transport fluxes.

These equations, describing species transport fluxes through a solid polymer electrolyte membrane are to be coupled with the equations, yet to be developed, describing mass transfer through the electrode porous backing layers and species mass transport with electrochemical/chemical kinetics in the porous electrode layers. The coupled equations, describing the various phenomena occurring in a DMFC in operation, will be of immense significance in the evaluation of performance and design/development of a DMFC.

The developed transport equations, in this report, can be used to experimentally determine the transport properties of a membrane, from very dilute to very concentrated solutions, such as permeability of the fluid mixture and effective mass diffusivities of the various species.