

Electroosmotic Flow in PEM Fuel Cells with Variable Zeta Potential

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Abstract

Water management is critically important for polymer electrolyte membrane (PEM) fuel cells, and is complicated by electroosmotic flow of water from anode to cathode through the polymer electrolyte membrane. In this work, the characteristics of electroosmotic flow in a Nafion[®] membrane with non-uniform zeta potential were investigated. The Poisson-Boltzmann and Navier-Stokes equations were used to model electrical double layer and the flow fields, respectively. The numerical results show the distorted electroosmotic velocity profiles resulting from the axial variation of the zeta potential.

Keywords: electroosmotic flow, zeta potential, PEM fuel cell.

1. Introduction

Polymer electrolyte membrane (PEM) fuel cell is one of the most promising candidates as zero emission power sources for both stationary and mobile applications. The electrolyte is an ion conducting polymer and transport protons generated during the anodic oxidation of fuel to the cathode. Perfluorinated sulphonic membranes, such as Nafion[®], are the ionomeric materials typically used in PEM fuel cells. The presence of the negative sulphonic charges on the wall surfaces of the nano-sized pores of the membrane results in the formation of a concentration gradient of protons close to the wall surfaces leading to a potential distribution in the electrolyte. This region is referred to as electric double layer, EDL. When subjected to the electrical field of an operating cell (e.g. in the range of about 3000 V/m), a significant electrokinetic body force will be developed, moving protons in the pores and dragging with them water molecules along the membrane. This phenomenon called electroosmotic flow, (EOF), increases the membrane resistance and degrades fuel cell performance [1].

The driving force for the EOF depends on the potential at the wall, referred to as zeta potential, ζ , and the strength of the applied electrical field. In general, zeta potential is a function of the ionic valence, the ionic concentration of the electrolyte solution, and the surface properties of the channel wall [2]. For a system with a simple electrolyte solution and a homogeneous channel wall, the zeta potential may be considered constant [3, 4]. As intuitively expected, these studies show that the EOF characteristics depend strongly on the value of the zeta potential. However non-uniform zeta potential distributions are commonly encountered due to impurities in the wall material, manufacturing defects, wall-adsorbed species, and variation in the solution pH. Although several researchers have investigated the effects of variable zeta potential on the EOF [5-8], to the knowledge of the authors, the study of EOF in Nafion[®] membrane is very limited.

Figure 1 depicts schematically the mechanism of water transport in a PEM fuel cell. Water can enter to the anode and cathode if the fuel and oxidant are partially humidified. Also, water is produced in the cathode due to the oxygen reduction. Inside the membrane, water is transported in two ways: EOF and back diffusion from cathode to anode. Since the EOF increases the membrane resistance and reduces fuel cell performance, it is very important to determine and manage the extent of EOF in the membrane to optimize the PEM fuel cell performance.

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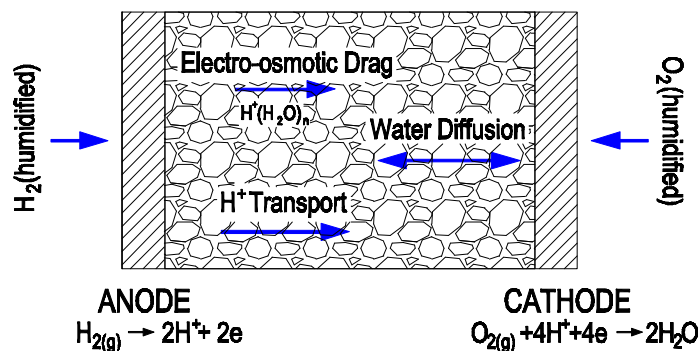


Fig. 1. Schematic of water transport and electroosmotic flow through the polymer electrolyte membrane in a PEM fuel cell.

The objective of this paper is to investigate the EOF in the electrolyte membrane with variable zeta potential. The Poisson–Boltzmann and the Navier–Stokes equations are solved numerically to study the electroosmotic flow in the membrane for which zeta potential decreases linearly from anode to cathode.

2. Governing equations

2.1. The charge distributions

According to the theory of electrostatic, the relationship between the electrical potential, $\psi(r)$, and the local volumetric net-charge density, ρ_e , is described by the Poisson equation [3]:

$$\nabla \cdot (\epsilon \nabla \psi) = -\frac{\rho_e}{e_0} \quad (1)$$

Where ϵ is the dimensionless dielectric constant of the electrolyte, and ϵ_0 is the permittivity of vacuum. A dielectric saturation model was developed by Paddison and Paul for fully hydrated Nafion[®] membranes. Based on their model, variations of dielectric constant as a function of distance from the pore wall, η , can be approximated mathematically as [3]:

$$\epsilon = \begin{cases} 17 & \eta \leq 7.8 \text{ \AA} \\ 17 + 23.7(\eta - 7.8) & 7.8 < \eta \leq 10.5 \text{ \AA} \\ 81 & \eta > 10.5 \text{ \AA} \end{cases} \quad (2)$$

The net-charge density for the proton-conducting membrane used in PEM fuel cell can be expressed in terms of the Boltzmann distribution as [3]:

$$\rho_e = z e n_\infty \exp\left(\frac{-ze}{k_B T} \psi\right) \quad (3)$$

Where z is the valence of the dissolved ions (H^+ , $z=+1$), n_∞ is the ionic number concentration in the bulk solution, e is the fundamental electronic charge, k_B is Boltzmann's constant, and T is the absolute temperature. Substitution of Eq. (3) into Eq. (1) and transforming it into non-dimensional form results in the Poisson-Boltzmann equation as follows:

$$\frac{1}{r^*} \frac{d}{dr^*} \left(r^* \frac{d\psi^*}{dr^*} \right) = -\frac{1}{2} (ka)^2 \exp(-\psi^*) \quad (4)$$

The non-dimensional variables are defined as:

$$\psi^* = \frac{\psi}{(k_B T)/(ze)} \quad \text{and} \quad r^* = \frac{r}{a} \quad (5)$$

Where r is the radial distance, a is the pore radius, and κ is Deby-Huckle parameter, which is a measure of the diffuse layer thickness and defined as [3]:

$$k = \left(\frac{2n_{\infty} z^2 e^2}{\epsilon \epsilon_0 k_B T} \right)^{1/2} \quad (6)$$

The boundary conditions for Eq. (4) are as follows:

$$\text{at } r^* = 0, \frac{dy^*}{dr^*} = 0; \text{ and at } r^* = 1, y^* = \frac{z}{(k_B T)/(ze)} \quad (7)$$

The equation of electrical potential is a nonlinear partial differential equation that must be solved numerically. A finite volume scheme with variable cell spacing was developed to discretize the equation. To facilitate convergence, the exponential term has been linearized as follows:

$$\exp(-y_{n+1}^*) = \exp(-y_n^*) - \exp(-y_n^*)(y_{n+1}^* - y_n^*) \quad (8)$$

Where n refers to the iteration number. The resulting system of algebraic equations was solved using the Gauss-Seidel iterative technique, with successive overrelaxation employed to improve the convergence time. The pore length was divide into identical segments in axial direction while the grid spacings are reduced successively to condense the control volume sizes in the region near the wall, where the electroosmotic effect is significant.

2.3. The velocity distributions

The Navier-Stokes equations for a Newtonian laminar liquid flow with constant density, ρ , and viscosity, μ , in a horizontal cylindrical capillary under the influence of an external electric force can be expressed as [3]:

$$m\nabla^2 u - \nabla p + F_E = 0 \quad (9)$$

representing the balance among the net viscous force, pressure force, and electric force acting on the fluid particles for the steady flow under consideration. The electric force is related to the charge density, ρ_e , and electric field strength, E as $F_E = \rho_e E$.

Eq. (9) can be non-dimensionalized as:

$$\frac{1}{r^*} \frac{d}{dr^*} \left(r^* \frac{du^*}{dr^*} \right) + F_P^* + F_E^* = 0 \quad (10)$$

Where u^* is the liquid velocity normalized with some reference velocity, U , considered as 1 mm.s^{-1} throughout this work. F_P^* and F_E^* are non-dimensional pressure and electroosmotic body forces, respectively, defined as:

$$F_P^* = \frac{\Delta P a^2}{mU}, F_E^* = M^* r_e^* E^* \quad (11)$$

$$\text{and } M^* = \frac{ze n_{\infty} z a^2}{mUL}, E^* = \frac{EL}{z}, r_e^* = \frac{r_e}{ze n_{\infty}} = \exp(-y^*) \quad (12)$$

Where L is the pore length. Eq. (10) is subject to the following boundary conditions:

$$\text{at } r^* = 0, \frac{du^*}{dr^*} = 0; \text{ and at } r^* = 1, u^* = u_s^* = Kn \frac{\partial u_s^*}{\partial n} \quad (13)$$

Where u_s^* is the dimensionless slip velocity and $Kn = \delta/a$ is Knudsen number and lattice spacing, δ , is about 3 \AA for water [3].

Now, consider two successive equal-size segments along the pore, each with a different zeta potential, and suppose that the high zeta potential segment is in the downstream and the low zeta potential segment is in the upstream. The liquid in the downstream segment would have a higher electroosmotic velocity, and the liquid in the upstream would have a lower electroosmotic velocity. This will cause different flow rate in different segments violating the continuity condition. The practical solution is that a vacuum tends to form between these two segments since the liquid in the downstream segment is moving faster than that in the

upstream segment. This will induce a negative pressure between these two segments, and slow the flow in downstream segment and increase the flow in upstream segment. In this way, the continuity condition will be satisfied. This is also why Eq. (10) has an induced pressure gradient term.

The resulting potential distributions are inserted into Eq. (10) to obtain the flow fields. The induced pressure gradient term in Eq. (2) will introduce more complexity into the numerical solution. To tackle this issue, Eq. (2) is initially solved numerically for the first and second sections by guessing an induced pressure gradient. The pore velocity profile is then obtained by solving the resulting tridiagonal matrix using a Thomas algorithm. Since the volumetric flow rates in the first and second segments must be identical, the induced pressure gradient in the second segment is corrected by the Newton-Raphson method, and used as an initial input for the third section. This technique is continued until the pressure gradient in the last segment is determined. For the same anode and cathode pressures (i.e., atmospheric pressure), the following equation must be satisfied:

$$\Delta P = \int \frac{\partial P}{\partial L} dL = 0 \quad (14)$$

The initially assumed pressure gradient needs to be revised several times until a complete convergence is achieved.

3. Results and discussions

The above equations and the matching boundary conditions for the EDL field and the flow field are solved numerically. All of the simulations are based on fully hydrated Nafion[®] membrane under the condition that the water content of the membrane on the anode side is sufficiently high to replenish the water and maintain the membrane hydration. The parameters and physical properties used in the simulation are listed in Table 1.

Table 1
Parameters and properties used in the present PEM simulations

Quantity	Value
Cell temperature	80 °C
Pore water viscosity	$3.6 \times 10^{-4} \text{ kg.m}^{-1}.\text{s}^{-1}$
Pore water density	980 kg.m^{-3}
Cell voltage	0.70 V
Fixed charge site concentration	$1.2 \times 10^{-3} \text{ mol.cm}^{-3}$
Wet membrane thickness	$2.31 \times 10^{-4} \text{ m}$
Pore diameter	$5 \times 10^{-9} \text{ m}$

Figure 2 shows the velocity field in a single pore with a linearly decreasing zeta potential from 150 mV to 50 mV. For a simple EOF in a nanochannel with uniform zeta potential, the plug-like velocity profile is expected. However, if the zeta potential is non-uniform, such as specified in this work, the net-charge density within liquid varies axially. Meanwhile, the applied electrical field strength, which depends on the electrical current and the conductivity of the electrolyte solution, is constant axially. Consequently, the electrical body force generating the EOF, which depends on the net-charge density and the electrical field strength, is different from segment to segment. In order to achieve the same flow rate as that in the next segment, with a higher zeta potential, a negative pressure gradient (the pressure decreases in the flow direction) is introduced to increase the flow rate. As shown in Figure 3, the pressure starts decreasing from a maximum pressure to the atmospheric pressure at the exit.

As shown in Figure 2, for the segments with higher zeta potentials, the electroosmotic velocity profile is distorted by the positive pressure gradient. The velocity fields are changing from Couette-type flow at the pore inlet to the plug flow at the middle of the pore and

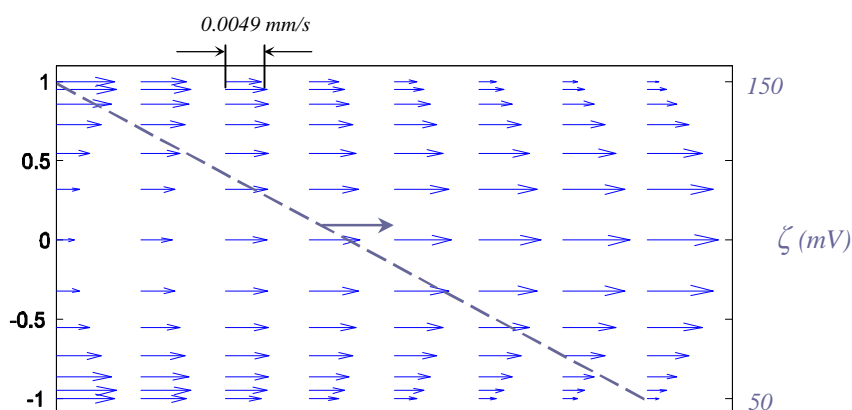


Fig. 2. The velocity field

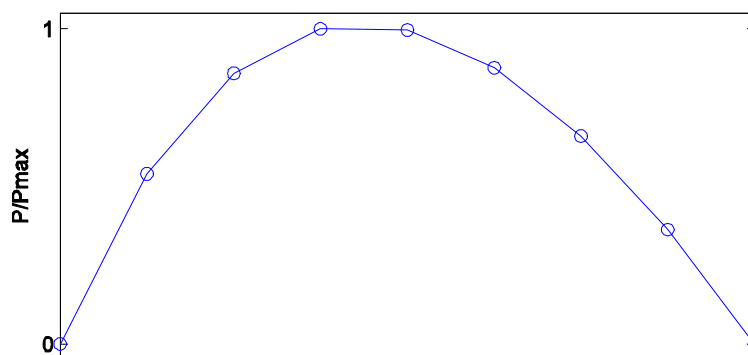


Fig. 3. Pressure distribution in pore length

eventually to the near-parabolic distributions at the pore outlet, as the zeta potential decreases and the induced pressure gradient prevails along the axial direction.

4. Conclusion

The Poisson-Boltzmann and Navier-Stokes equations are solved numerically to determine the electroosmotic flow in a Nafion[®] membrane with non-uniform zeta potential distribution. The results show that the different types of velocity profiles are developed along the membrane. The present results can be used to study the effects of the membrane surface characteristics on the electroosmotic drag in PEM fuel cells.

Nomenclature

a	pore radius (m)	U	reference velocity (e.g. 1 mm.s ⁻¹)
e	fundamental electronic charge (1.602×10 ⁻¹⁹ C)	u^*	non-dimensional velocity
E	electric field strength (V.m ⁻¹)	u_s^*	non-dimensional slip velocity
E^*	non-dimensional term	z	valence of the dissolved ions
F_E^*	dimensionless electroosmotic force	<i>Greek letters</i>	
F_P^*	non-dimensional pressure force	ε	dimensionless dielectric constant
Kn	Knudsen number = δ/a	ε_0	permittivity of vacuum (8.85×10 ⁻¹² C ² .N ⁻¹ .m ⁻²)
k_B	Boltzmann constant (1.381×10 ⁻²³ J.K ⁻¹)	κ	Debye-Huckel parameter (m ⁻¹)
L	pore length (m)	μ	viscosity (Pa.s)
M^*	non-dimensional term	η	distance from the pore wall (Å)
n	iteration number	ψ	potential (V)
n_∞	bulk ionic number concentration (m ⁻³)	ψ^*	non-dimensional potential
P	pressure (Pa)	ρ	density (kg.m ⁻³)
P_{max}	maximum pressure (Pa)	ρ_e	net volumetric charge density (C.m ⁻³)
r	pore radius (m)	δ	lattice spacing (e.g. 3×10 ⁻¹⁰)
r^*	non-dimensional pore radius	Δ	difference
T	temperature (K)	ζ	zeta potential (V)

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