

An overview of electro-osmosis in fuel cell polymer electrolytes

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Abstract

Electro-osmosis, the transport of water with protons, in polymer electrolyte fuel cell membranes is important because it effects water management within an operating cell on both a global and local level. The electro-osmotic drag coefficient is the number of water molecules transported per proton and is a quantitative measure of the extent to which electro-osmosis occurs in a given polymer electrolyte. The methods for which electro-osmotic drag coefficients have been determined are reported. An effort is made to report proton electro-osmotic drag coefficients extensively, while a few non-proton cation electro-osmotic drag coefficients have been chosen for illustrative purposes. The results reported have implications for fuel cell performance and in the development and characterization of new polymer electrolyte membranes.

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Keywords: Fuel cell; Polymer electrolyte; Electro-osmosis

1. Introduction

When an electric field is applied across an ion containing membrane, ions move through the membrane due to electro-motive forces. This ion transport is accompanied by solvent transport through the membrane. Solvent is transported either by an association with the transported ion, such as a hydration sphere, or by hydrodynamic pumping due to the movement of the ions and associated solvent molecules. This solvent transport accompanying the ion transport through a membrane is termed electro-osmosis. The number of solvent molecules carried per ion is the electro-osmotic drag coefficient, and is used as a measure of the extent to which electro-osmosis occurs in a given ion/membrane/solvent system. In fuel cell applications, protons are the ions of interest and water is the solvent of interest, and for the purposes of this paper, electro-osmosis and the electro-osmotic drag coefficient will refer to water flux due to proton flux or the number of water molecules carried per proton, unless otherwise noted.

Electro-osmosis results from proton chemistry. Because isolated protons lack any electron cloud, they do not exist as free species in solution [1]. Instead, protons interact with the electron density of neighboring water molecules, forming dynamic species consisting of aggregates of water molecules and an excess proton (i.e. H_3O^+ , H_5O_2^+ (Zundel ion), or H_9O_4^+

(Eigen ion)). Proton transport in these solutions is believed to occur by two competing mechanisms: the vehicle mechanism and the Grotthuss ‘hopping’ mechanism [1]. Illustrations demonstrating the difference between the two mechanisms are shown in Fig. 1. The vehicle mechanism occurs by the movement of the hydrated proton aggregate through the aqueous environment, in a process similar to molecular diffusion. The Grotthuss mechanism involves the ‘hopping’ of a proton down a chain of hydrogen bonded water molecules. The hops are followed by reorientation of the water molecules. True proton conduction within a polymer electrolyte membrane involves a competition between these two mechanisms. In this regard, proton electro-osmotic drag coefficients are different than most other ions (Na^+ , K^+ , Cl^- , etc.) because hopping mechanisms are not possible.

Electro-osmotic drag is significant in fuel cells because it directly impacts water management. At a local level, it can affect hydration of the polymer electrolyte and the electrodes. The hydration in turn affects the conductivity of most fuel cell membranes [2–4], and hence the ohmic losses within a cell. Additionally, high water content within the electrodes can accelerate electrode kinetics [5]. However, if water content is too great, the electrodes become flooded, retarding mass transport to the electrodes significantly lowering cell performance.

Electro-osmosis also affects system level issues in fuel cells. Feed gas flow rates and pressures must be set to ensure that cells remain properly hydrated but not flooded, which often requires that reactant streams be humidified. Thermal management of the stack can be influenced by electro-osmotic drag due to effects of evaporative cooling. These factors affect

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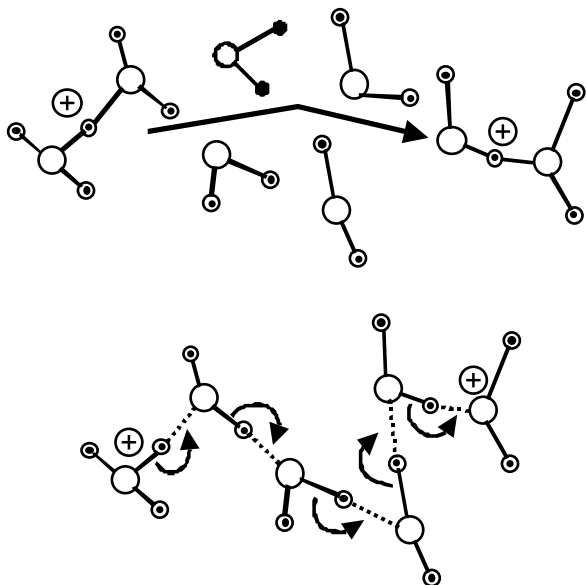


Fig. 1. Schematic of proton transport mechanisms; (top) the vehicle mechanism, (bottom) the Grotthuss or hopping mechanism.

peripherals, such as water condensers or make up water, adding weight and parasitic energy requirements to the system. For low power direct methanol fuel cell systems, electro-osmotic drag can limit system power density [6].

Beyond the direct fuel cell effects related to water management, electro-osmosis has also been related to selectivity of direct methanol fuel cell electrolytes and been used to infer microstructural information about alternative electrolytes [7–9].

Having established the importance of electro-osmosis in relation to fuel cell performance, an overview of electro-osmosis in the literature is presented. This overview focuses on the experimental techniques that have been used to determine electro-osmotic drag coefficients, the conditions under which these experiments have been run, and the resulting experimentally determined drag coefficients. To this point, no such overview exists in the literature and will prove useful for those looking to explore electro-osmosis, particularly for fuel cells but also in other applications (such as electrodialysis).

2. Background

While electro-osmotic drag has a significant impact on fuel cell performance, it has not been investigated to the same extent that other fuel cell relevant transport properties (such as conductivity, permeability or water self-diffusion coefficient) have. There are many reasons for this. At issue are the complex experimental apparatus needed for many of the techniques, length of time or difficulty required for set-up and/or measurement, mechanical or chemical stability of test membranes, complex data interpretation and/or difficulty applying measured parameters to fuel cell performance. The exact difficulties depend on the specific technique used for obtaining electro-osmotic drag.

A number of different techniques for determining electro-osmotic drag coefficients have been reported. Table 1 represents a comprehensive list of the data available in the literature for proton electro-osmotic drag coefficients through polymers. A few entries have been added for other cation electro-osmotic drag coefficients for reference. The entries in Table 1 have been separated in terms of the experimental factors controlled during the experiment and the physical quantity measured to determine the electro-osmotic drag coefficient. This allows for the arbitrary separation of these techniques into broader categories or classes that will be discussed in greater detail in the body of this paper.

The techniques used have been categorized into the following categories: the electro-osmotic drag cell, the radio-tracer drag cell, fuel cell or fuel cell-like cells, streaming potential measurements, the activity gradient method, electrophoretic NMR, and scanning electrochemical microscopy. Depending on the type of experimental apparatus used, different membrane conditions can be investigated. For example many of the techniques require added electrolyte, while others are done in equilibrium with water vapor.

A discussion of each of the individual methods follows. Each method is reviewed in terms of the experimental apparatus and test conditions. Experimental results and advantages and disadvantages of each technique are presented.

3. Discussion

3.1. The electro-osmotic drag cell

The electro-osmotic drag cell is the most straight-forward method for determining electro-osmotic drag coefficients. The current is controlled and the flux of solvent is measured. The electro-osmotic drag cell was the first method used for determining electro-osmotic drag coefficients. In this type of cell, shown in Fig. 2, a membrane is placed vertically between two solution-filled compartments, and electrodes placed in each compartment drive a current through the membrane. The flux of ions created by the electrodes is accompanied by a flux of solvent through the membrane. A change of volume of each compartment is recorded as a function of the current passed. After taking into account any volume changes due to the electrode reactions, electro-osmotic drag coefficients are calculated [10].

In theory, the flux of solvent per ion is easily obtainable; however, this method can be experimentally difficult, as the volume changes measured are generally small. This means that any reaction involving the production or consumption of gas phase species makes measuring this change difficult or impossible. Changes in liquid density due to cell temperature fluctuations can also affect the experimentally obtained coefficients. These factors limit the choice of the electrodes and solutions that can be used for obtaining electro-osmotic drag coefficients and add uncertainty to experimentally obtained electro-osmotic drag coefficients.

An additional limitation of this method is the use of an added electrolyte. Added electrolyte is generally necessary to

Table 1
Literature references for proton electro-osmotic drag coefficients and techniques

Technique (driving force)	Measured quality	Aqueous solution	Membrane	Proton drag coefficient	Non-proton drag coefficient	Cell electrodes	Source
Electro-osmotic drug cell (applied potential)	Volume change	Halogenic salts	Anion/cation exchange	2.6–2.77	Many	Ag/AgCl	Breslau and Miller, 1971
		DI water	Nafion 117, Membrane C, Dow experimental	0.9, 2.0–2.9, 2.6–4.0, 1.4–2.0		Pd/Pd-H	Zawodzinski et al., 1993 (two papers)
		KCl	Cation exchange			9–11 (K ⁺)	Ag/AgCl
Radiotracer method (applied potential)	Isotope concentration	H ₂ SO ₄ , H ₃ PO ₄ , HCl	Nafion 117, Cation, Polybenzimidazole	3–8, 1.5–2.3, 0–1.05		Pd/Pd-H	Pivovar et al., 2005
		H ₂ SO ₄	Nafion 117	3.2–8		Pt/H ₂ O	Verbrugge and Hill, 1998
Fuel cell (electro-chemical)	Water crossover	MeOH	Nafion 117, Membrane C, Dow experimental	2.0–5.1, 3.0–5.0, 2.0–3.1		Pt–Ru anode, Pt cathode	Ren et al., 1997; 2001
		MeOH	Nafion, BPSH, sPI, 6FCN	3.3–3.9, 1.4–3.0, 0.5–0.8, 1.3		Pt–Ru anode, Pt cathode	Pivovar et al., 2001; Hickner, 2003; Kim et al., 2004
Hydrogen pump (applied potential)	Pressure change	Vapour	Nafion 117/H ₃ PO ₄ , PBI/H ₃ PO ₄	0.2–0.6, <0.01–0.09		Pt anode, Pt cathode	Weng et al., 1996
Electrolysis (applied potential)	Unclear, likely water crossover	HCl	Nafion	0.2–9.5		High surface area/catalytic	Balko et al., 1981
Streaming potential (applied pressure)	Water crossover	HCl/water vapor	Nafion 115	3.5–3.8	Many	Pt anode, Pt cathode	Motupally et al., 2002
		Electro-chemical potential	Halogenic salts	Cation/anion exchange			Ag/AgCl
Activity gradient (chemical potential)	Electro-chemical potential	HCl/KCl	Cation exchange	2.3	11.2	Ag/AgCl	Okada et al., 1992
		Vapour	Nafion 117	1.4		Pt–H ₂	Fuller and Newman, 1992
Electrophoretic NMR (applied potential)	NMR shift	DI water	Nafion 117, Membrane C, Dow experimental	1.0, 1.1, 0.95		Pt–H ₂	Zawodzinski et al., 1995
		SECM (applied potential)	Conc. of electro-active species	NaCl	Nafion	1.5–2.8, 0.5–50	Pt–H ₂ O
					3.7–6.4 (Na ⁺)	Ag/AgCl	Bath et al., 1998

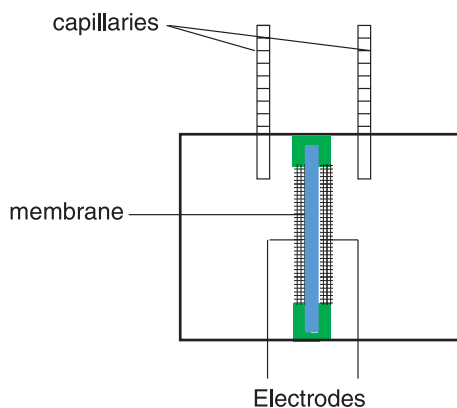


Fig. 2. Schematic of the experimental electro-osmotic drag cell.

allow ion conduction between the electrodes and test membrane. This added electrolyte can affect the observed electro-osmotic drag, as electro-osmotic drag coefficients have been shown to be a strongly dependent on electrolyte concentration [7,10,11]. Additionally, the type of electrolyte has been found to effect the measured electro-osmotic drag coefficient [7]. This dependence on type and concentration of added electrolyte can make the experimentally obtained electro-osmotic drag coefficients difficult to apply to fuel cell conditions when no added electrolyte is present.

While this method does have limitations, it has been used extensively for determining electro-osmotic drag coefficients of cations other than protons (see Ref. [10] for review and list of references). However, the use of this method to determine proton electro-osmotic drag coefficients has been limited. Bresslau and Miller obtained a proton electro-osmotic drag coefficient of $2.6 \text{ H}_2\text{O}/\text{H}^+$ through a homogeneous polystyrene sulfonic acid membrane made by Asahi Chemical Company using this method [12]. They used silver–silver chloride electrodes and solutions of 0.1 M hydrochloric acid. In this set-up, the silver–silver chloride electrodes react to either release or absorb a chloride ion. Protons within the cell then migrate through the membrane to satisfy electro-neutrality within each cell compartment. This results in a concentration polarization across the membrane, because as the experiment progresses the concentration of hydrochloric acid in each compartment becomes unequal. This creates an osmotic driving force that distorts the interpretation of the data.

Zawodzinski et al. overcame this concentration polarization effect by using palladium–palladium hydride electrodes [4,13]. These electrodes are able to absorb and release protons because of the high solubility of hydrogen in palladium and the catalytic nature of palladium to hydrogen oxidation/reduction. These researchers hot pressed palladium–palladium hydride electrodes into the membranes being tested. This eliminated the need for added (free) electrolyte in the test cell as ionic contact was made directly from the electrodes to the membrane. In this way they eliminate the need for added electrolyte and were able to more closely mimic operating conditions of a liquid saturated fuel cell electrolyte. These researchers investigated electro-osmotic drag coefficients through three different

perfluorosulfonic acid ionomers at 30 °C. Experimental uncertainty of these experiments seemed to be fairly high as drag coefficients were found to be between 2.0 and 2.9 for Nafion; 2.6 and 4.0 for Membrane C; and 1.4 and 2.0 for Dow membrane. The authors also reported a drag coefficient (0.9) based on a single measurement for lower water content Nafion (11 rather than 22 $\text{H}_2\text{O}/\text{sulfonic acid group}$). However, the reproducibility of this data point are unclear based on the technique used.

Another series of experiments by Mayer and Woermann investigated the transport of non-electrolytes through the membrane due to electro-osmotic drag [14]. These researchers worked with cation exchange membranes made from the condensation reaction of *p*-phenolsulfonic acid and formaldehyde. Current was driven through the membrane using silver–silver chloride electrodes in contact with a potassium chloride solution. The electro-osmotic drag coefficients obtained were for potassium ions rather than protons, so they are not directly relevant for fuel cell applications. However, these researchers studied the transport of urea, sucrose and raffinose due to electro-osmotic flow. While not presented in this study, the transport of methanol another, non-electrolyte, is relevant for issues of methanol crossover in the operation of direct methanol fuel cells, and has been investigated by Barragan et al. using a similar approach [15].

Pivovar et al. modified the cell design of Mayer and Woermann by replacing the silver–silver chloride electrodes with palladium–palladium hydride electrodes and adding membrane supports to the membrane mount [7]. The membrane supports prevented deflection of the test membranes allowing more accurate measurements, and the use of palladium–palladium hydride electrodes had two major advantages over silver–silver chloride electrodes. First, because the transference number of the protons in these systems was near unity, electrodes that consumed and produced protons reduced concentration polarization. This simplified data analysis and reduced experimental uncertainty. Second, because the silver–silver chloride electrodes required chloride ions in solution, the system was limited to hydrochloric acid. In contrast, the palladium–palladium hydride electrodes worked effectively in any acid, allowing anion effects to be investigated simply by varying the type of acid used in the experiment. During this work, these researchers studied the electro-osmotic drag coefficients of Nafion, CR61 CMP (crosslinked polystyrene sulfonic acid) and polybenzimidazole (PBI) in contact with sulfuric, phosphoric or hydrochloric acid from 0.01 to 1.0 M. They found strong differences in the electro-osmotic drag coefficient of Nafion based on type of acid and concentration. CR61 CMP showed relatively little change in electro-osmotic drag coefficient regardless of operating conditions. Nafion had the highest reported drag coefficient (> 3), CR61 CMP had a moderate drag coefficient (~ 2) and PBI had a low drag coefficient (> 1). Interestingly, a polymer without incorporated acid groups (PBI) was able to be tested for electro-osmotic drag due to the presence of added electrolyte. These authors also examined anion partition coefficients, conductivity, water uptake,

methanol permeability and transference numbers. They attributed the differences in observed properties to chemical and structural effects of the membranes, and demonstrated the utility of electro-osmotic drag coefficients as a function of added electrolyte and concentration as a probe for polymer microstructure.

3.2. The radiotracer drag cell

The radiotracer drag cell operates in a manner similar to the electro-osmotic drag cell. The primary differences in the two techniques are the physical quantities measured. In both cells, an ionic current is driven through test membranes resulting in electro-osmotic flow. In the electro-osmotic drag cell, the volume or mass of the transferred solution is measured. In the radiotracer drag cell, it is the concentration of an added isotope that is measured. The reported use of this experiment started by spiking the anode compartment with a sample of water containing tritium, ^3H , rather than hydrogen, ^1H . Charting the concentration of tritium versus time and current passed allowed for the extraction of electro-osmotic drag coefficients [11].

Like the electro-osmotic drag cell, the radiotracer drag cell requires an electrolyte in solution to provide the ionic conductivity necessary to test reasonable current densities. However, this method offers a major advantage over the electro-osmotic drag cell in that gas phase reactions at the electrodes can be tolerated, eliminating the need for electrodes that avoid gas phase species and allowing a variety of electrolytes to be used. On the down side, this approach requires both tritium (a radioactive species) and a scintillation counter. In the only reference to this technique in the literature for electro-osmotic drag coefficients, Verbrugge and Hill investigated Nafion in sulfuric acid and found electro-osmotic drag coefficients to be a function of concentration, with values from 3 to 8 $\text{H}_2\text{O}/\text{H}^+$ [11].

3.3. Membrane-electrode assembly cells

Membrane-electrode assembly cells, which include fuel cells, hydrogen pumps and electrolysis, are another method that has been used to obtain electro-osmotic drag coefficients. What separates this particular approach is that test membranes are made into membrane-electrode assemblies (MEAs), in which electrodes containing catalyst particles and ionomer are bonded to the test membrane. These MEAs are the heart of any polymer electrolyte fuel cell, and those investigated for electro-osmotic drag are often tested directly as fuel cells, where reactants (thus far only methanol has been demonstrated) and oxidants (oxygen or air) provide the electrochemical driving force for proton flux. However, the driving force for proton flux can also be applied externally through a power supply, such as in the case of hydrogen pumps or electrolysis.

A significant advantage to these approaches is that fuel cell hardware, often available in labs where electro-osmotic drag is a concern, can be adapted rather easily to obtain experimental drag coefficients. Further advantages of these techniques are

that the measurements taken from a functioning fuel cell or under fuel cell relevant conditions are easily applied to fuel cell performance, and fuel cell hardware is made to operate at a controlled temperature allowing relatively easy acquisition of temperature dependent data. A disadvantage of this technique is that membranes tested need the ability to be made into reasonably well performing MEAs, as reasonably high current densities need to be reached in order to isolate diffusion and electro-osmotic contributions to water flux. This usually requires that sample sizes be of reasonable size and that high performance electrodes can be bonded to the membranes. The MEAs must also remain stable over the time frame of the experiment, a challenge for some hydrocarbon membranes like those commonly employed in electro-dialysis based on polystyrene sulfonic acid. Finally, data at multiple current densities may need to be obtained in order to decouple the effects of water transport by diffusion and electro-osmosis.

Fuel cell derived electro-osmotic drag coefficients have only been reported with methanol as the fuel; however, these measurements would also be possible using other fuels such as hydrogen. For the direct methanol fuel cell derived electro-osmotic drag coefficients, protons produced from the oxidation of methanol are carried through the membrane by an electrochemical potential gradient and react with oxygen to form water at the cathode. Water and methanol also pass through the membrane by a combination of electro-osmosis and diffusion. The water in the cathode exit gas stream is collected and measured as a function of the current passed through the membrane. The amount of methanol reacting at the cathode is determined by monitoring CO_2 concentration in the cathode effluent. The amount of water passed through the membrane due to diffusion and electro-osmotic flow is found after subtracting the water produced from the reaction of protons and methanol at the anode. By obtaining data points at high current density where the effects of diffusion are negligible, an electro-osmotic drag coefficient can be calculated.

A direct methanol fuel cell was first employed to determine electro-osmotic drag coefficients of Nafion by Ren et al. [16]. In this study, the electro-osmotic drag coefficient of Nafion was found to be a strong function of temperature, ranging from 2.0 $\text{H}_2\text{O}/\text{H}^+$ at 15 °C to 5.1 $\text{H}_2\text{O}/\text{H}^+$ at 130 °C. These researchers later expanded their investigation to include Nafion of alternative equivalent weight, and Dow Experimental membrane and Asahi Membrane C (two other perfluorosulfonic acid polymers) [17]. The data for Nafion showed a clear trend of increasing electro-osmotic drag coefficient with decreasing equivalent weight. Membrane C showed the highest electro-osmotic drag of any of the membranes tested, while the Dow membrane showed the lowest drag in spite of its relatively low equivalent weight. The temperature dependence of electro-osmotic drag coefficients for all the membranes tested was very similar.

This method has also been employed to the study of sulfonated poly(arylene ether sulfone) copolymers, BPSH, sPI and 6FCN in Table 1 [8,18,19]. These wholly aromatic polymers have shown good durability in fuel cell tests and

improved performance as direct methanol fuel cell electrolytes [20]. Their electro-osmotic drag coefficients have been investigated as a function of sulfonation level, backbone chemistry and temperature. Similar to the results for perfluorosulfonic acid ionomers in the work on Ren and Gottesfeld, these aromatic hydrocarbon polymers exhibited increasing electro-osmotic drag coefficients with increasing sulfonic acid content and increasing temperature [17,18]. Increased relative selectivity for direct methanol fuel cell performance of these membranes has been related to decreasing electro-osmotic drag coefficient within a family of these copolymers with decreasing sulfonation level [8]. In general, these polymers have shown much lower electro-osmotic drag coefficients than Nafion, a potential advantage when considering system issues involving humidification requirements. The method for this work is essentially that proposed by Ren et al. [16], however, one study also demonstrated the viability of humidified feed gases in reducing the importance of diffusion in these systems, a potentially important result in applying this technique to hydrogen fuel cells [19].

Other electro-chemical cells similar to fuel cells have also been used to determine electro-osmotic drag coefficients. For example, A hydrogen pump has been used to measure electro-osmotic drag coefficients through Nafion and polybenzimidazole (PBI) containing sorbed phosphoric acid at temperatures near 200 °C [21]. This cell, shown in Fig. 3, used the test MEA to separate two compartments containing both hydrogen and water. A potential was applied across the MEA causing hydrogen in the anode compartment to be oxidized to protons and transported through the MEA to the cathode where it was reduced back to hydrogen, hence the term ‘hydrogen pump’. At the elevated temperatures used in this experiment, all the water transported through the MEA due to electro-osmosis is vaporized. Electro-osmotic drag coefficients were calculated from the pressure change of each compartment as a function of current passed. Phosphoric acid was needed in the PBI system because PBI does not conduct in an undoped state. Phosphoric acid was also needed in the Nafion system, because Nafion dehydrates and is poorly conducting at these elevated temperatures. The reported drag coefficients are very low, < 0.1 for PBI and between 0.2 and 0.6 for Nafion. Because of the

very high temperatures and low water content, these data are of limited interest for traditional polymer electrolyte membrane fuel cells, but may be of interest for phosphoric acid fuel cells, particularly PBI-phosphoric acid cells.

Electrolysis of halogenic acids is another method that has been used to report electro-osmotic drag coefficients. Electro-osmotic drag coefficients for Nafion between 0.2 and 9.5 were reported by Balko et al., apparently in contact with various concentration HCl solutions [22]. However, the reference gives little information on how the experiments were run or how the effects of diffusion effected the reported drag coefficient, making the data presented of little if any value. This approach was expanded upon by Motupally et al. [23]. These researches input gas phase HCl into their electrolysis cell and measured water flux across the cell as a function of current density. The experiment was performed at an HCl flow rate where the diffusion flux was found to be constant. The linear response of water flux versus current density was proportional to the observed electro-osmotic drag coefficient, and reported to be 3.84 at 80 °C and 3.5 at 60 °C. These numbers are in good agreement with results run in direct methanol fuel cells at similar temperatures. An added disadvantage of this approach is the need to handle halogenic acids as a reactant.

3.4. Streaming potential measurements

Streaming potential measurements represent the first method presented in which water flux in some way is not measured in order to determine electro-osmotic drag coefficients. Streaming potential measurements are made in cells similar to the one shown in Fig. 4. In this cell, a membrane separates two solution filled compartments. The two compartments contain electrodes that can be used to pass current through the membrane, so this design is similar to the electro-osmotic drag cell, Fig. 2. However, the similarity between these two methods ends here. In a streaming potential measurement, a pressure gradient is imposed across the membrane by attaching one of the solution compartments to a pressure head, while venting the other compartment to the atmosphere (or some other controlled pressure). The electrodes in the streaming potential cell are not used to pass current

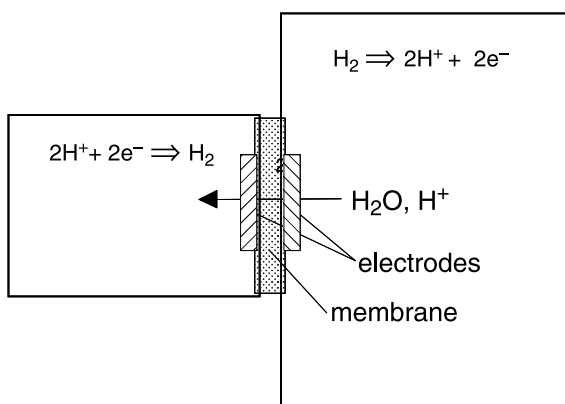


Fig. 3. Schematic of the hydrogen pump cell.

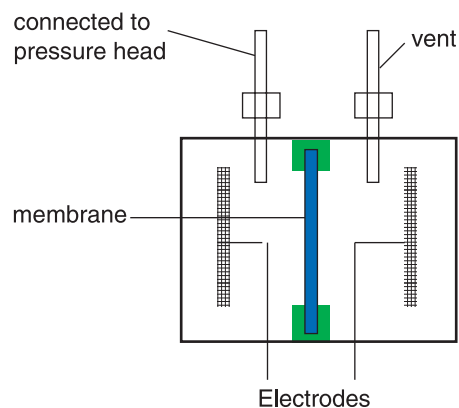


Fig. 4. Schematic of the streaming potential cell.

through the membrane, but they measure the potential drop between the two electrodes created by this pressure gradient. This measured potential difference between the two electrodes is termed the streaming potential, and can be used to determine electro-osmotic drag coefficients [24–26]. The equations used to extrapolate the electro-osmotic drag coefficients from experimental data are complex and beyond the discussion presented here (see Ref. [25]).

This experiment has been used extensively to determine electro-osmotic drag coefficients of cations other than protons through ion exchange membranes. Only a single reference for a proton electro-osmotic drag coefficient was found using this technique [26]. In this reference, the authors tested a polystyrene sulfonic acid membrane, CR61 AZL (Ionics, Inc.) in 0.03 M HCl. A drawback of this technique, much like the electro-osmotic drag cell, is that it requires the use of an added electrolyte; however, concentration polarization can be eliminated using this technique by extrapolating a plot of the measured potential drop versus the square root of time to zero [25].

It is worth noting, although no literature reference on the subject could be found, that in theory this measurement could be run in reverse using appropriate electrodes and electrolyte. For this ‘reverse’ streaming potential measurement, a controlled potential would be applied across the membrane and the resulting pressure head would be measured. The same equations used for traditional streaming potential measurements could then be employed to determine electro-osmotic drag coefficients of this ‘reverse’ streaming potential measurement.

3.5. Activity gradient method

The activity gradient method is another method that has been used to determine electro-osmotic drag coefficients. An activity gradient cell is shown in Fig. 5. In this type of cell, a membrane is placed between two cell chambers and held above solutions of different water activity (lithium chloride solutions of different concentrations have been used in the examples presented here). At each end of the membrane there is a platinum electrode. The membrane and the electrodes are kept in contact with hydrogen and water vapor in equilibrium with the solution in the cell compartment. The water activity gradient between the two compartments results in a driving

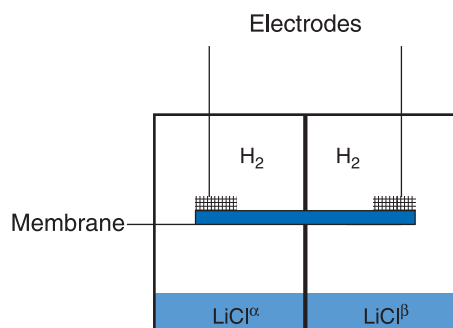


Fig. 5. Schematic of the activity gradient cell.

force for water molecules through the membrane from one compartment to the other. This creates a potential difference between the two electrodes that is related to electro-osmotic drag, see Ref. [27] for details. By measuring the potential difference across the cell as a function of the ratio of water activities in the two test chambers, electro-osmotic drag coefficients are obtained.

Fuller and Newman first employed this method to determine the electro-osmotic drag coefficient of Nafion in equilibrium with water vapor [27]. These researchers reported the electro-osmotic drag coefficient of Nafion as a function of water content between 0 and 14 water molecules per sulfonic acid site. They reported that for water contents above 4 water molecules per sulfonic acid site, that the drag coefficient was constant at 1.4 for Nafion. For water contents below 4 water molecules per sulfonic acid site, they reported a nearly linear decrease in drag coefficient with decreasing water content. Zawodzinski et al. used this method to measure the electro-osmotic drag coefficient of Nafion, Dow Experimental Membrane (Dow), and Membrane C (Asahi) [28]. These membranes, all perfluorosulfonic acid ionomers, have relatively similar chemical and physical properties. The results of Zawodzinski et al. are in moderate disagreement with those reported by Fuller and Newman. These researchers report a slightly lower drag coefficient (1.03) essentially constant for water contents between 2 and 14 water molecules per sulfonic acid site. The data reported by these researchers gives the electro-osmotic drag coefficients of the Dow membrane as 0.95 and Membrane C as 1.1. The electro-osmotic drag coefficients reported here for the perfluorosulfonic acid ionomers although smaller follow the same trends as those reported by Ren and Gottesfeld [17] for liquid equilibrated samples tested in a direct methanol fuel cell.

The primary observation from these works is that vapor equilibrated (lower water content) perfluorosulfonic acid polymers exhibit significantly lower electro-osmotic drag coefficients than liquid equilibrated samples. This method has shown utility at low degrees of hydration, like those found in hydrogen fuel cells, and possibly of interest for cells at high temperature/low humidity or at sub-freezing conditions. However, the experiments and data processing can be time consuming and tedious, and this approach has not been demonstrated in liquid equilibrated systems.

3.6. Electrophoretic NMR

Electrophoretic nuclear magnetic resonance (NMR) is an additional method that has been used to determine electro-osmotic drag coefficients [29,30]. So far this technique has been limited to the work of Kreuer et al. due in part to the complicated experimental apparatus and data manipulation required. This method also suffers from relatively large experimental uncertainties. This technique involves driving an ionic current through a membrane by an applied electrochemical potential within an NMR probe. This ion flux creates an electro-osmotic flow in the same direction. This electro-osmotic flow causes a phase shift of the NMR signal that

depends on the magnitude of the electro-osmotic drag coefficient. Electro-osmotic drag coefficients can be determined by the interpretation of these signal shifts, see Ref. [29] for further details.

These researchers investigated electro-osmotic drag coefficients of Nafion and sulfonated poly(ether ether ketone) (PEEK) as a function of hydration level and temperature. The data obtained using this technique show good agreement for electro-osmotic drag coefficients with other published values for Nafion as a function of temperature. Nafion electro-osmotic drag coefficients varied from 1.5 to 2.8 depending on degree of hydration and temperature. PEEK drag coefficients had a much wider range from 0.5 to 5.0. PEEK exhibited higher water uptake than Nafion, but had significantly lower electro-osmotic drag coefficients at similar water to sulfonic acid contents.

This technique has the advantage of being able to be run with either a vapor or liquid phase. Because the technique involves electrodes that are in direct contact with the test membrane, added electrolyte is not required to pass current although the measurements can also be made in the presence of added electrolyte. The flexibility of operating at varying degrees of hydration is a great advantage of this technique as it can simulate the environment in both gas and liquid feed fuel cell systems.

3.7. Scanning electrochemical microscopy

Scanning electrochemical microscopy is the final technique presented that has been used to estimate electro-osmotic drag coefficients. This method, shown schematically in Fig. 6, is based on positioning a scanning electrochemical microscope (SECM) tip directly above a membrane and detecting electro-active molecules as they pass through the membrane. Ions, driven through the membrane by electrodes in the adjacent compartments, carry electro-active molecules through the membrane by electro-osmotic convection. Electro-osmotic drag coefficients are calculated by measuring the current at the SECM tip as a function of the current passed across the membrane [31].

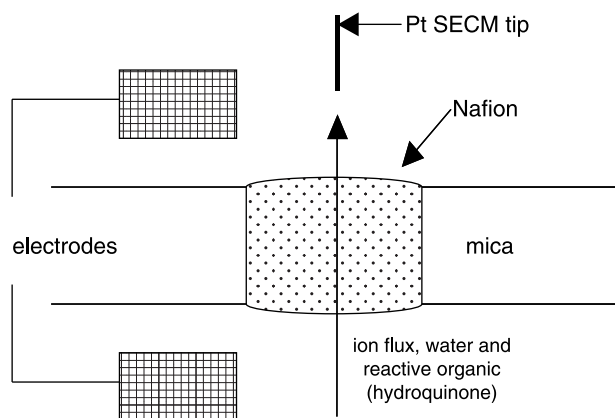


Fig. 6. Schematic of the scanning electrochemical microscopy cell.

This method requires an added electrolyte in solution to carry the ionic current through the membrane. While SECM has commonly been used in the investigation of catalysts and corrosion; only a single report exists using this technique to obtain electro-osmotic drag coefficients [31]. The authors only investigated the electro-osmotic drag of sodium ions through Nafion. This technique is not as reliable as other techniques because it contains many assumptions about the transport of the electro-active species, but it does represent another reported technique for determining electro-osmotic drag coefficients.

4. Summary

An overview of the techniques presented for obtaining electro-osmotic drag coefficients has been presented, with special emphasis on polymer electrolyte fuel cell applications. Each method has been reviewed in terms of the experimental apparatus and test conditions. Experimental results and advantages and disadvantages of each technique were presented.

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