

Hypothesis

On the Nature of Electro-Osmotic Drag

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Abstract: Electro-osmotic drag (EOD) is usually thought of as a transport mechanism of water inside and through the polymer electrolyte membrane (PEM) in electrochemical devices. However, it has already been shown that the transport of dissolved water in the PEM occurs exclusively via diffusion, provided that the EOD coefficient n_d is constant. Consequently, EOD is not a water transport mechanism inside the electrolyte membrane, and this means that its nature is not yet understood. This work proposes a theory that suggests that the root of the EOD is located in the catalyst layers of the electrochemical device where the electric current is generated, and consequently could be linked to one or more of the elementary reaction steps. It is therefore also conceivable that EOD exists at one electrode in an electrochemical device, but not in the other. Moreover, the EOD coefficient n_d may depend on the current density as well as the oxidization level of the catalyst. The last consequence, if EOD is linked to an elementary reactions step, it could also be part of the rate-determining elementary step, and this could open pathways to increase the reaction kinetics by finding ways of enhancing the water/hydronium ion transport out of or into the polymer phase.

Keywords: electro-osmotic drag; polymer electrolyte membrane; proton exchange membrane fuel cells; proton exchange membrane electrolyzer cells; membrane water transport; elementary reactions steps; rate-determining step

1. Introduction

As we are entering the hydrogen age, proton exchange membrane fuel cells (PEMFCs) and electrolyzer cells (PEMECs) play a central role because of their high efficiencies and their noiseless and clean operation [1]. These technologies can be ideally paired with intermittent power sources such as wind energy or solar energy to create a carbon-free future energy system, using hydrogen and electricity as “energy currencies”. The synergy of electricity and hydrogen was pointed out by Scott and Häfele [1], and is illustrated along with the conversion technologies in Figure 1.

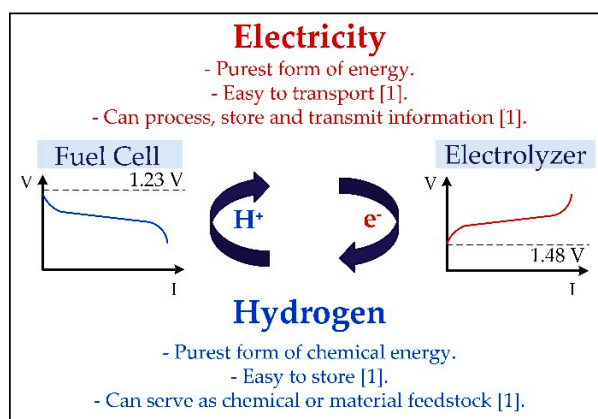
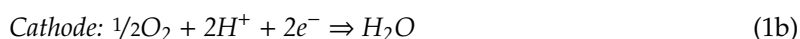


Figure 1. The “H⁺–e[−] Cycle” of polymer electrolyte membrane (PEM) fuel cells and electrolyzers.

In order to adopt a widespread use of these “neat hydrogen” technologies, however, it is imperative to make these technologies economically attractive, and this requires further improvements and fundamental understanding.

A PEMFC converts hydrogen fuel and oxygen from air into electricity. Air is fed to the cathode side of the cell while hydrogen is supplied to the anode. Oxygen and hydrogen are transported through the porous gas diffusion layers towards the catalyst layers where the electrochemical reactions occur, driven by the electromotive force of the fuel cell and local overpotentials that are the main source of waste heat (e.g., [2]). At the anode catalyst layer (ACL), hydrogen is split into protons that migrate through the polymer electrolyte membrane (PEM) towards the cathode catalyst layer (CCL) where the protons recombine with electrons and oxygen to create water. The electrons travel through the external cycle and thus provide electricity.

The half-cell reactions are therefore:



The theoretical, ideal voltage of a fuel cell can be calculated out of Gibbs free energy of the overall reaction to be 1.23 V at standard conditions [2]. In a PEM electrolyzer cell, the opposite reactions take place, and electricity must be supplied to the cells. Waste heat is usually produced here as well, and the basis for the calculation of the electrolyzer efficiency is the thermoneutral voltage, calculated out of the enthalpy of reaction, and this is 1.48 V at standard conditions [2].

For the low-temperature PEM technology, the membrane must be kept in a hydrated state while at the same time cell flooding must be avoided [3,4], which requires a careful adjustment of the operating conditions [5,6]. The water management of the fuel cell or electrolyzer cell in general and of the membrane in particular need to be fundamentally understood and the various water transport mechanisms carefully studied.

2. Water Transport Inside a Polymer Electrolyte Membrane

This section presents a brief overview of water transport mechanisms and important properties. It is, however, far from being a complete literature review, as only the most important aspects are highlighted.

A comprehensive review of the various water management issues in fuel cells, as it was state of the art at that time, was published by Dai et al. [7]. A central question in both PEMFCs and PEMECs is how the water actually crosses the membrane. The traditional view is that water crosses the membrane predominantly by the following mechanisms [3,7]:

- (1) Electro-osmotic drag (EOD), always directed from anode to cathode;
- (2) Diffusion (earlier also named “back diffusion”), typically assumed from cathode to anode in PEMFCs and from anode to cathode in PEMECs;
- (3) Hydraulic permeation from the high-pressure half-cell to the low-pressure half-cell.

Voss et al. [8] at Ballard Power Systems conducted detailed experiments and concluded that diffusion appears to be a dominant process. In that work, the authors proposed to remove excess water by the anode gas stream by imposing a concentration gradient across the membrane to counterbalance the effect of EOD, thus only considering the first two effects from above, as the pressure difference across the membrane in their work was low. The hydraulic permeation was usually considered negligible, except for the work by Bernardi and Verbrugge [9,10], who employed the Schlögl equation, which balances hydraulic permeation with a water flux driven by a potential gradient.

It is important to realize that an important transport mechanism is missing in the list above, and this is the nonequilibrium sorption (NES) of water to/from the membrane from/to the surrounding

gas/liquid phase, because any water that crosses through the membrane must first be adsorbed by the membrane. No calculation or fundamental understanding of water crossing the membrane can be complete without accounting for this effect, as was already shown in previous work [11].

The conservation equation for water inside the electrolyte phase in a fuel cell is [12]:

$$\frac{\rho^{mem}}{EW} \nabla \cdot (D_{w,mem} \nabla \lambda_w) = \nabla \cdot (n_d \frac{I}{F}) - \alpha \times k_a \times \frac{\rho^{mem}}{EW} (\lambda_{w,equil} - \lambda_w) \quad (2)$$

Diffusion = EOD - NES

This equation is the conserved form of the electrolyte water transport as it is typically employed in a computational fluid dynamics (CFD) model, and it is mathematically equivalent to a flux balance that accounts for the same phenomena. In Equation (2), the diffusion term consists of the membrane density ρ^{mem} , the membrane equivalent weight EW , and the diffusion coefficient of water inside the membrane $D_{w,mem}$. The EOD term consists of the drag coefficient n_d , the current I , and the Faraday constant $F = 96,485$ C/mole. Finally, the nonequilibrium sorption (NES) term is proportional to the area density of the electrolyte phase inside the catalyst layer α [m^2/m^3], a kinetic absorption/desorption coefficient k_a , and the membrane density ρ^{mem} divided by the equivalent weight of the membrane EW . The driving force for absorption/desorption is the deviation of the membrane water content λ_w from its equilibrium value $\lambda_{w,equil}$, and the latter depends on the relative humidity of the adjacent gas phase [3].

A similar expression was employed by Lu et al. [13] in their CFD model of a PEMFC. However, that group included the hydraulic permeation term while neglecting the NES term. This was also done in the original model by Springer et al. [14], who considered only the diffusion term and EOD. Note that the hydraulic permeation term was also included in the modeling work of our group [15], but this term was applied to undissolved, “free” water inside the membrane, and not to the water that had dissolved into the electrolyte phase. The hydraulic permeability is a strong function of the membrane water content [16,17], but it was found that the overall effect is negligible compared to the terms in Equation (2) [12]. This, however, appears to be different for electrolyzers that are sometimes operated with a high pressure gradient [18].

In their groundbreaking research, Springer et al. [14] developed a model for water transport in a PEMFC membrane where they assumed that the membrane is always in equilibrium with the neighboring gas/liquid phase, thus $\lambda_{w,equil} = \lambda_w$, and consequently the NES term would be identical to zero. This explicitly stated assumption in the model by Springer et al. [14] became for a long time an unstated, implicit assumption in many modeling attempts that followed. Even the commercial ANSYS Fluent Fuel Cell Module in its first version only accounted for EOD versus diffusion and neglected the NES term [19].

A key property in Equation (2) and for the overall understanding of membrane water transport is the EOD coefficient n_d . It was shown in a previous publication that when n_d is a constant, as it is frequently assumed (e.g., [20,21]), the picture of water transport through the electrolyte membrane can be simplified [11]. Under such conditions, the EOD term becomes identical to zero inside the membrane, and it is nonzero only inside the catalyst layers where the current is generated, and therefore the divergence of the current in Equation (2) is nonzero. A comparison between the traditional view of membrane water transport and the special case where n_d is a constant is shown in Figure 2. When neglecting hydraulic permeation, the only dissolved water transport mechanism inside the membrane is diffusion. Therefore, depending on whether n_d is a constant or not, there is a fundamental difference in the membrane water transport, and our understanding of it.

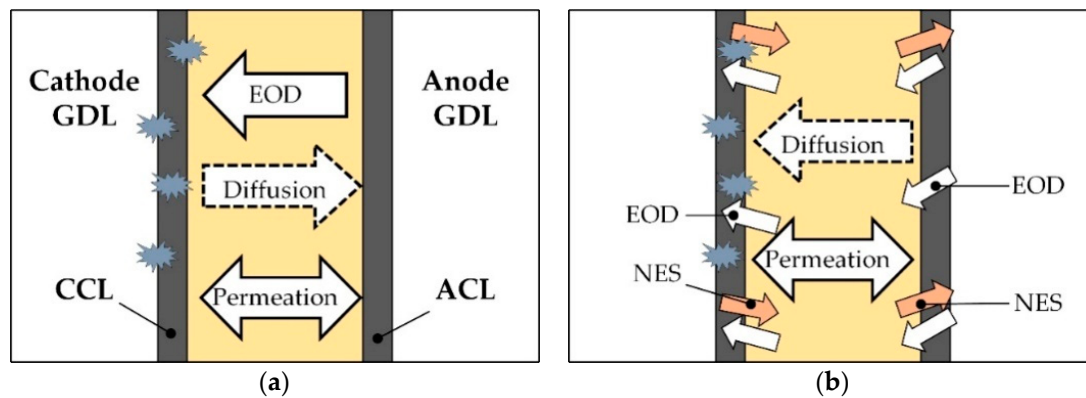


Figure 2. (a) Traditional view of membrane water transport. The stars denote water production in the cathode catalyst layer (CCL). (b) Alternative view of membrane water transport where the electro-osmotic drag (EOD) is a source/sink term of membrane water, and it is partly balanced by nonequilibrium sorption (NES). The difference between EOD and NES is the amount of water that diffuses through the membrane. Forward and backward diffusion are possible. In the alternative model, hydraulic permeation applies only to nondissolved water.

Consequently, a key task in our overall understanding of the membrane water transport is to determine the value of the EOD coefficient n_d , which is discussed in the next section.

3. The EOD Coefficient n_d

Because the value of n_d and the question whether it is constant or not is of central importance for the fundamental understanding of membrane water transport, literature on the determination of this value is briefly reviewed.

Zawodzinski et al. [3] first introduced the concept of λ as the number of water molecules per sulfuric acid group in a PEM. Depending on the water vapor activity of the adjacent gas phase, λ varies between 2 and 14, and when the membrane is equilibrated with liquid water, λ can be as high as 22. This group also found that important material properties such as the water diffusion coefficient in the membrane and the proton conductivity of the membrane exhibit a strong dependency on λ [3]. In their ensuing modeling paper, Springer et al. [14] formulated equations to describe water transport and calculate the overpotentials in a fuel cell. The applied Darken coefficient led to a spike in the water diffusion coefficient inside the membrane as function of λ , which was later on found to be a mathematical artifact owing to the fact that the curve-fit between the membrane water content and the water vapor activity in the adjacent gas phase was chosen to be cubic [22].

As for the EOD coefficient, Springer et al. [14] suggested a linear dependency between n_d and the membrane water content λ , according to

$$n_d = 2.5/22 \times \lambda. \quad (3)$$

The EOD coefficient n_d denotes the number of water molecules that are transported by each proton, i.e., an $n_d = 1$ means that each proton that crosses the membrane drags one water molecule along (it will be shown below that this picture is incorrect). An n_d value of unity thus means that twice the amount of water as is produced in the electrochemical reaction is transported through the membrane, caused by EOD.

The expression in Equation (3) was based on two measured data points: one for a membrane that was equilibrated with liquid water ($\lambda = 22$) that yielded a drag coefficient of $n_d = 2.5 + 0.3$, and one data point of $n_d = 0.9$, measured for a thermally treated, modified membrane with a water content of $\lambda = 11$ [14]. In that work, the authors were only able to obtain values for a membrane equilibrated with liquid water.

In 1992, Fuller and Newman [23] published values for the EOD coefficient based on a concentration cell experiment and analyzed their results using transport equations derived from concentration solution theory. They reported a constant value of $n_d = 1.4$ for a partially hydrated membrane. This value decreased to zero in the range $0 < \lambda < 3$. The resulting curve as was shown in reference [23] exhibits a remarkable resemblance to the shape of the diffusion coefficient as a function of the membrane water content, as proposed by our group [22].

Recognizing the advantage of the concentration cell as constructed by Fuller and Newman, i.e., that n_d values over a wide range of activity values could be obtained, Zawodzinski et al. [24] constructed a similar experimental setup. Instead of calculating the resulting EOD coefficients with equations derived from concentration theory, however, they applied a somewhat simpler but not less elegant approach, arguing that the passage of protons themselves does not lead to a change in free energy, and thus the only change in free energy is caused by water molecules crossing the membrane [24]. By correlating the change in free energy with the difference in water vapor activity between the electrodes, the EOD coefficient could be calculated out of the measured cell potential. These authors now calculated a constant n_d value of unity for all water vapor activities of a partially hydrated membrane. All experiments by Fuller and Newman [23] as well as Zawodzinski et al. [24] were conducted at room temperature.

Therefore, from the early work experiments by Fuller and Newman [23] as well as the Los Alamos group, it may be concluded that the resulting EOD coefficient was $n_d = 1$. In particular, the Los Alamos group corrected their own initial assumption made in the Springer paper [14] of having a linear dependency between n_d and the membrane water content. In that light, it is difficult to understand why the expression for the EOD coefficient according to Equation (3) is still widely employed, even in modern modeling studies as well as in commercial computational packages.

In 1999, Ise et al. [25] conducted an electrophoretic NMR and employed the laws of irreversible thermodynamics in order to isolate and determine the EOD coefficient. This method was very complex and the error bars fairly large, and the resulting drag coefficients were between 1.5 and 2.5 for Nafion at room temperature and at membrane hydration values of $\lambda = 11$ and higher, suggesting that 3–5 times the amount of product water would cross the membrane due to EOD. They also gave a very good overview of the experiments that had been done to determine n_d , and they pointed out that some results were contradictory.

Later on, a different experiment to measure the EOD coefficient was conducted by Ye and Wang [26], who used a hydrogen pumping cell and obtained constant n_d values of around 1.07 over a wide range of membrane water contents.

It is beyond the scope of this work to go into more details in all ensuing studies that attempted to measure the EOD coefficient, and a comprehensive overview of the various experimental efforts was given by Pivovar [27]. However, it should be stated that in numerous studies, authors attempted to measure the EOD coefficient by eliminating diffusion inside the membrane. For this purpose, the membrane was often equilibrated on both sides with liquid water. According to the prior reasoning of this author, it is impossible to eliminate diffusion and still have water crossing the membrane. Admittedly, in the experiments by Ye and Wang [26], the membrane was also equilibrated with water on both sides while the measured n_d coefficient was close to unity and constant.

Another critical comment is that in some studies the electro-osmotic drag coefficient appears to have been confused with the net drag coefficient of water crossing the membrane, r_d , defined as:

$$r_d = \frac{\dot{n}_{H_2O}^{an,in} - \dot{n}_{H_2O}^{an,out}}{I/F}, \quad (4)$$

where I is the total current drawn from the cell and F is Faraday's constant (96,485 C/mol). The molar fluxes are the water fluxes at the inlet and outlet of the anode side of the fuel cell.

A different experiment to isolate the EOD coefficient in an operating fuel cell was suggested in reference [11]. As argued above, inside the catalyst layers the EOD stands in competition to the NES

term, and the difference between these two terms is the water that is condensed into or evaporated out of the membrane phase. Following this argumentation, one arrives at the conclusion that if the NES term can be suppressed, then the net drag coefficient of the water that crosses the membrane (via diffusion) must be equal to the EOD coefficient, $r_d = n_d$ (see Figure 2b).

The NES term depends on the specific surface area of the electrolyte phase inside the catalyst layers and a kinetic adsorption coefficient that depends on the temperature according to the Arrhenius equation [28]. Therefore, in order to measure n_d directly in an operating fuel cell, one should build a membrane-electrode assembly with a very low electrolyte loading in the cathode catalyst and ideally conduct these experiments at a low temperature owing to the Arrhenius type of dependency. On the other hand, sufficient water has to be provided to the anode side in order to sustain an expected net drag coefficient of unity or higher. According to previous calculations, the anode side humidifier has to be operated at 85 °C and hydrogen has to be supplied at a stoichiometric flow ratio of 1.5 or higher to provide a sufficient amount of water [29]. The high temperature would make it difficult to reduce the NES term to a negligible amount, but a strong effect of the electrolyte loading in the CCL on the water balance can be expected. The overall fuel cell water balance can then be accurately measured with a hot wire anemometer [29,30].

As it was already pointed out above, the fact that n_d could be a constant has very important practical implications. Even if we limit our considerations for the moment to the membrane water content range, where n_d was found to be unity [24], then we are left with a membrane water transport picture as shown in Figure 2b. For the sake of clarity, this is now repeated:

The EOD is confined to the electrodes, and this effect is in part balanced by the nonequilibrium sorption. The difference between these two terms is the amount of water that diffuses through the membrane. Any dissolved water that crosses the membrane diffuses through it [11]. Mathematically, the EOD term becomes a source/sink term for membrane water from/to the adjacent gas or liquid phase, and this makes the EOD an interface effect, similar to the NES term. Consequently, even inside the electrodes it holds that the water transport inside the electrolyte phase is via diffusion. This is in contrast to the frequently drawn picture of an actual dragging of water by protons through the membrane. The difference between the EOD term and the NES term, i.e., the right side in Equation (2), is the amount of water that condenses into or evaporates from the electrolyte phase as this water undergoes a phase change with detectable evaporation/condensation energy.

Experiments to measure the transversal membrane water profile in a fuel cell during operation have shed some light into the question as to how the water crosses the membrane. However, it is beyond the scope of the present work to summarize the numerous different studies that were conducted in the past. It is only pointed out that as early as 1996, Mosdale et al. [31] had clear indication that even when current is crossing the membrane, the water redistributes in a diffusion-like process. Moreover, later on the same group from CEA Grenoble employed confocal Raman spectroscopy and showed that the water concentration gradient inside the membrane can also point from anode to cathode [32], thereby eliminating the concept of “back diffusion”. The measured water profile in the membrane was also near linear, which is in good agreement with CFD simulations by our group [12], but in vast contrast to early modeling results by Eikerling et al. [20].

To sum up: when the EOD coefficient n_d is constant, the only fundamental water transport mechanism inside the electrolyte phase is diffusion. This is the case for a large range of membrane water content values of up to $\lambda = 14$ [24], i.e., when the membrane is equilibrated with water vapor. Once, however, one is committed to applying a constant n_d and thereby arriving at diffusion-only water transport, it is difficult to see why this fundamental transport mechanism inside the membrane should change just because the boundary condition for the water activity may change. Either the EOD is a fundamental water transport mechanism inside the membrane, or it is not. This author claims the latter. This leads to the question concerning the nature of EOD:

If EOD is not a water transport mechanism inside the polymer electrolyte membrane, what is it instead?

In order to obtain a better view of the nature of EOD, a number of hypotheses are formulated below, which lead to a completely different understanding of EOD that is more coherent with the mathematical equations.

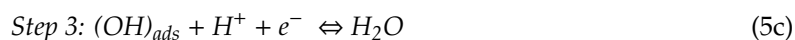
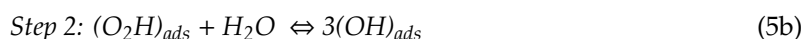
4. Hypotheses on the Nature of EOD

In the following, a picture of the EOD will be drawn that contrasts with conventional thinking. In the beginning, the only assumption is to have a constant value for n_d .

The previous argumentation arrived at the conclusion that EOD is an interface effect confined to the fuel cell (or electrolyzer) electrodes. It is similar in nature to the nonequilibrium sorption term, but different in that it is mathematically connected to the generation/consumption of electrical current. Mathematics dictate that where there is current generated or consumed, there is electro-osmotic drag.

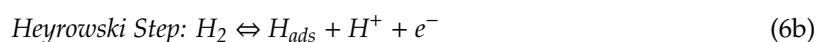
In order to better understand the nature of EOD, it is therefore instructive to investigate other phenomena that occur inside the electrodes and are connected to the generation of current. The other phenomena that occur inside the catalyst layers are the electrochemical half-cell reactions. It is known that these half-cell reactions occur in a frequency of elementary reaction steps, and in order to find the origin of EOD, it is therefore instructive to analyze these elementary reaction steps. While it is beyond the scope of this work to expand on the vast number of studies and literature on this highly complex subject, the very accessible overview and introduction to the physics of elementary reaction steps given by Koper [33] is pointed out.

For the oxygen reduction reaction that occurs in the cathode of a PEMFC, the most accepted mechanism is:



Step 1 and Step 3 were confirmed by Damjanovic and Brusic [34], and the first step was identified as the rate-controlling one. These authors also listed numerous alternative reaction mechanisms both for oxygen evolution and dissolution [34]. It is known that the reaction mechanisms may change depending on whether or not the electrode is oxide-covered, and the above mechanism was proposed for an oxide-free electrode. According to the review by Koper, it is generally believed that in electrolyzers, the steps follow in reverse order [33]. Note that in a recent paper, Reier et al. [35] stated that for the electrocatalytic oxygen evolution as it occurs in electrolyzers, none of the oxygen evolution reactions have been fully validated.

The most accepted pathway for the hydrogen oxidation reaction in acid is (e.g., [36,37]):



While many of these elementary reaction steps have been formulated with protons, it has been stated elsewhere that protons usually do not exist as free species in a solution [38], and other authors have written the reverse hydrogen evolution reaction with hydronium ions instead of protons (e.g., [39]).

The reason why these elementary reactions steps in PEMFC and PEMEC are brought up in this work that focuses on the nature of EOD, is that in fact the root cause for EOD may be found in the elementary reaction steps. It was shown above that EOD can be tracked down to the catalyst layers, and it is the next logical step to connect the EOD to the current-generating steps inside the catalyst layers as well, as it is mathematically already connected to them. Consequently, the following hypotheses are formulated:

Hypothesis 1. *EOD is not a water transport mechanism inside polymer electrolyte membranes.*

Hypothesis 2. *EOD is an interface effect and connected to the current generation in the electrodes.*

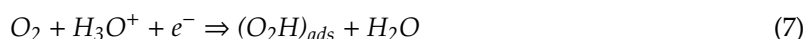
Hypothesis 3. *The EOD coefficient n_d can have a different value in the electrodes.*

Hypothesis 4. *The EOD coefficient n_d can depend on the current density and the catalytic surface.*

5. Discussion

Hypothesis 1 was already stated in previous work [11], albeit not as a hypothesis, and is only repeated here for the sake of completion. The only transport mechanism of dissolved water inside the electrolyte phase is diffusion.

Hypothesis 2 requires elaboration. The EOD coefficient may be linked to the other current-generating phenomena, i.e., the elementary reaction steps. Consequently, future research should focus on identifying the elementary reaction steps that cause EOD. It is generally difficult to see how an elementary reaction step that involves dragging a water molecule out of the electrolyte phase could be as facile as others. Damjanovic and Buric [34] have already found that the first step in the oxygen reduction reaction according to Equation (5a) is the rate-determining one. If this reaction step is written with a hydronium ion instead of a proton, it would look like:



Where the hydronium ion would be taken from the electrolyte phase, and, according to the effect of the EOD, the resulting water molecule would be located outside of the electrolyte phase. Likewise, the last step, Equation (5c), could also be written with hydronium ions to yield an additional water molecule on the right hand side of the equation. In this way, each proton/hydronium ion would bring a water molecule out of the electrolyte phase, and an EOD coefficient of unity could be explained.

Hypothesis 3 follows out of the fact that the half-cell reactions in a fuel cell or electrolyzer follow different reaction pathways. For this reason, it is also conceivable that EOD occurs in only one of the electrodes. The overall picture of membrane water transport as drawn here in Figure 2b would allow for such a scenario while the traditional view as drawn in Figure 2a would not. The “standard case” of implementing the EOD term as a source term for membrane water at the fuel cell anode side and a corresponding sink term for the cathode side was described in a previous publication [11], and it was possible to explain the observed water flow directions.

Hypothesis 4 follows out of the observation that the reaction pathways can change with current density and oxide coverage of the platinum catalysts [34].

As a final comment, it should be stated that the current view and hypotheses apply to water transport in the membrane and are therefore not in conflict with the typical view on proton transport through the membrane via two competing mechanisms, the vehicle transport mechanism and the Grotthuss “hopping” mechanism (e.g., [27]).

6. Conclusions

It can be concluded from this work that the EOD is not a transport mechanism for membrane water. Instead, it is a phenomenon that occurs only inside the catalyst layers and is (mathematically) connected to the current generation. As such, it is reasonable to propose that EOD should be linked to the elementary reaction steps. When analyzing the steps for the oxygen reduction reaction that occurs in PEMFC as proven experimentally by Damjanovic and Buric [34], it becomes obvious that when writing the first and last elementary steps with hydronium ions rather than protons, water is brought from inside the electrolyte phase to the outside. Thus, EOD is proposed to be a part of the elementary reactions steps. As it is difficult to see, how the EOD mechanisms could be as facile as other elementary reactions steps, it is also proposed that EOD is part of the rate-determining step. Because anode and

cathode follow different elementary reaction steps in PEMFC and PEMEC, it is then suggested that EOD can occur in one electrode, but not in the other. Finally, it is known that the elementary reaction steps depend on the catalyst surface treatment as well as the current density, and therefore the EOD may also vary with these conditions. This may help to explain the large variation of experimentally determined values for the EOD coefficient n_d .

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