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# Hydroxide Transport in Anion-Exchange Membranes for Alkaline Fuel Cells

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Additional information is available at the end of the chapter

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## Abstract

In this chapter are described the characteristics of transport of hydroxide ions through hydrated polymeric materials with potential application in alkaline fuel cells are described. First, it is made a brief description of anion-exchange membrane fuel cells (AEMFCs), their evolution and key characteristics. Then, this chapter presents a detailed classification of the different types of polymers that have been proposed for AEMFCs and their state of development. After that, mechanisms involved in the transport of hydroxide ions through hydrated anion-exchange membranes are described and discussed, making emphasis in the theoretical approaches applied for their study and their implementation and representability in global transport models. In the final section, it is summarized the key features of the chapter and is made a brief discussion about challenges and future work required for the consolidation of this promising technology.

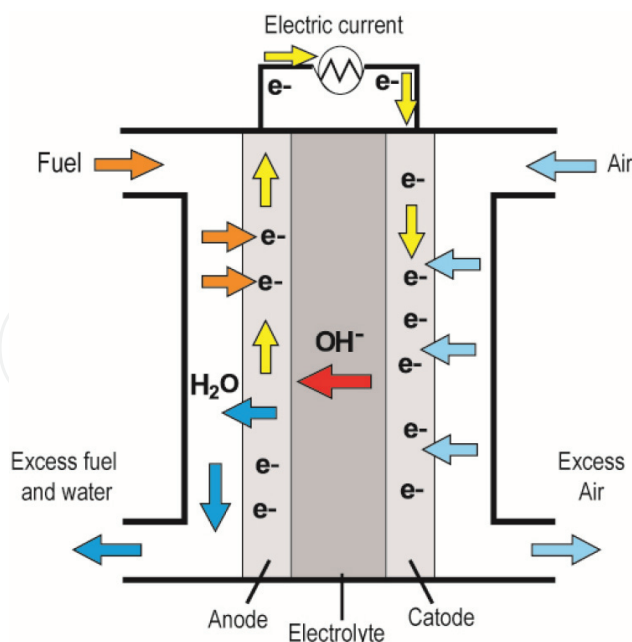
**Keywords:** fuel cell, anion-exchange, polymer, hydroxide ion, transport phenomena

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## 1. Introduction

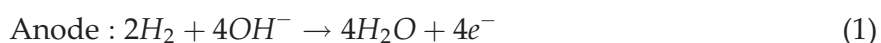
A fuel cell is a device that converts the chemical energy contained in a fuel directly and efficiently (between 60 and 80% at normal operating conditions) into electrical energy. This is achieved by the coupling of reduction/oxidation reactions between oxygen and fuel fed respectively to the cathode and anode of the cell, having as by-products water and CO<sub>2</sub> in low amounts when a hydrocarbon (such as methanol or ethanol) is the fuel [1, 2].

The general scheme of an alkaline fuel cell (AFC) is shown in **Figure 1**. In this device, fuel is oxidized at the anode and combined with hydroxide ions transported from the cathode



**Figure 1.** General scheme of an AFC.

through the electrolyte to produce water. Part of water leaves the cell while the rest moves through the electrolyte to the cathode. There, it is combined with oxygen and electrons coming from the anode through an external circuit to produce hydroxide ions that are then transported through the electrolyte to the anode [3–5]. The electrochemical reactions involved if the fuel is hydrogen are:



The most known types of AFCs use liquid solutions as electrolytes because of their high ionic conductivity [5, 6]. However, they have as disadvantage their short lifetime under normal operating conditions mainly due to the formation of carbonates ( $\text{CO}_3^{2-}$ ) between hydroxides of the electrolyte and  $\text{CO}_2$  [7–10] and the permeation of liquid electrolyte to electrodes (weeping) [10]. In consequence, polymer-based membranes for AFCs are developed and implemented [11, 12] following the model of their counterparts, the proton-exchange membrane fuel cells (PEMFCs). With this, the newly born AEMFCs were made suitable for their use in vehicles and batteries for mobile devices because of: (a) the conductive species of the electrolyte are integrated to a rigid polymeric matrix so reactivity and production of carbonates is reduced, (b) there is no weeping because the electrolyte is a solid whose segregation is minimum, and (c) the versatility of the fuel cell is better with respect to implementation and handling using the polymeric electrolyte [3, 6, 13].

Despite this, the polymeric materials used as electrolytes in AEMFCs currently show drawbacks susceptible of research and development in their ionic conductivity and chemical

stability. Such characteristics limit the efficiency and durability of the fuel cell respectively; thus, their study is the main focus of research in this area. Most of studies are experimental and focused on the fabrication and characterization of polymeric materials with potential application in AEMFCs. The others are theoretical and seek to represent transport phenomena of hydroxide ions through anion-exchange membranes to understand their characteristics and propose how to improve them. Therefore, this chapter is developed as follows: first, it reviews and discusses the contributions and findings made to date about anion-exchange membranes for AEMFCs from both experimental (Section 2) and theoretical studies (Section 3). Then, it addresses the challenges and work required to consolidate the AEMFCs and make them a feasible energy production technology for the close-future.

## 2. Experimental studies

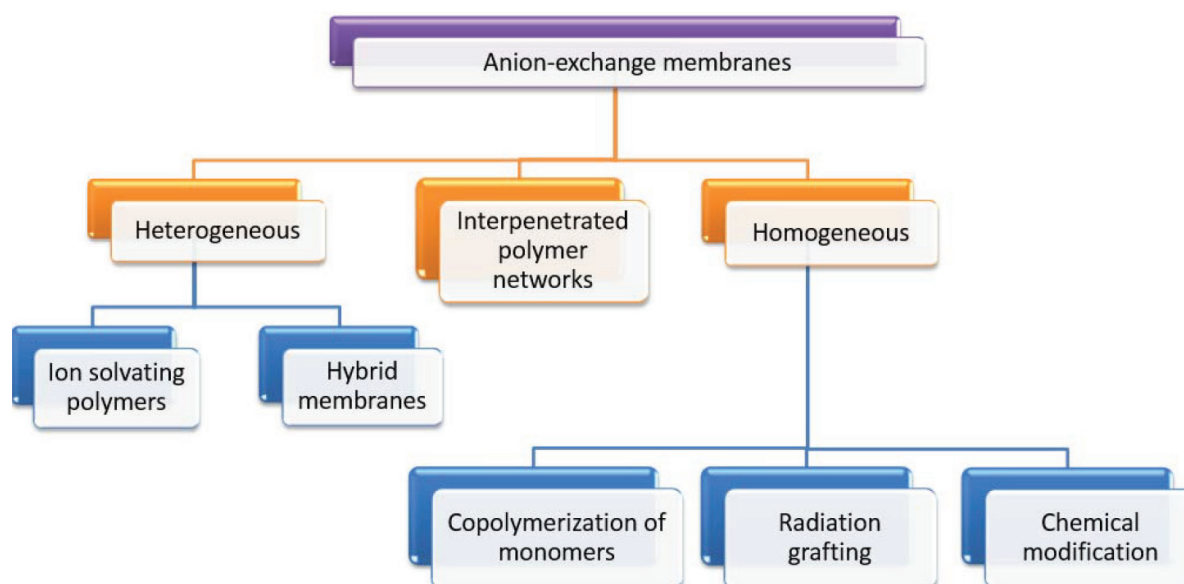
The experimental research of anion-exchange membranes for AEMFCs has focused on the development of materials having: (a) good mechanical and thermal properties at the assembly and operation conditions of the fuel cell [14–16], (b) chemical stability especially against the attack of hydroxide ions to the cationic functional groups of the membrane [17–19], (c) high anionic conductivity ( $>100$  mS/cm) [6, 20, 21], (d) electronic isolation [22], (e) appropriate thickness (between 50 and 80  $\mu\text{m}$ ) [3], (f) low permeability to fuel [9], and (g) low cost [23, 24]. In order to fulfill them, diverse anion-exchange membranes have been fabricated and studied. These membranes can be classified according to their structure as: (a) heterogeneous, subclassified according to the nature of their components, (b) interpenetrated polymer networks, and (c) homogeneous, subclassified according to their functionalization method [3]. This is schematically shown in **Figure 2**.

### 2.1. Heterogeneous membranes

A heterogeneous membrane is an anion-exchange material embedded in an inert compound. According to their nature, these membranes are classified into:

#### 2.1.1. Ion solvating polymers

They are composed of a polymeric matrix soluble in water that contains electronegative heteroatoms (such as oxygen, nitrogen, sulfurs, chlorides or phosphates), a hydroxide (most of the time potassium hydroxide) and one or more plasticizers. The resultant material has the mechanic properties of the polymeric matrix and the electrochemical properties of the hydroxide [25, 26]. Among the materials used to fabricate ion solvating polymers, there are the polyethylene oxide (PEO), polyvinyl alcohol (PVA), chitosan and polybenzimidazole (PBI). They have good mechanical properties but low ionic conductivity at contact with the fuel cell electrodes (between 0.1 and 1 mS/cm) [27] because they are usually very thick and have high electrical resistance. Moreover, their structure is usually not uniform and has areas of high and low concentrations of exchangeable ionic groups that cause an uneven ionic transport through



**Figure 2.** Classification of anion-exchange membranes according to their structure and functionalization method. Reprinted from *J. Memb. Sci.*, 377(1–2), G. Merle, M. Wessling, K. Nijmeijer, Anion exchange membranes for alkaline fuel cells: A review, 1–35, Copyright 2011, with permission from Elsevier.

the material. Additionally, the KOH used as a hydroxide is susceptible to leak out the membrane, resulting in continuous conductivity losses during the operation of the fuel cell [20].

### 2.1.2. Hybrid membranes

They are composed of organic and inorganic segments. Organic segments provide the electrochemical properties and the inorganic (usually silica or siloxane), the mechanical properties. Examples of hybrid membranes are PEO, PVA and polyphenylene oxide (PPO) with silica ( $\text{SiO}_2$ ) and membranes based on PVA with titanium dioxide ( $\text{TiO}_2$ ). Although their mechanical properties are promising due to the incorporation of inorganic components, membranes of this category have the same nonuniformity problem of ion solvating polymers, thus their ionic conductivity are similar or even lower [15].

## 2.2. Interpenetrated polymer networks

These membranes combine two polymeric materials by crosslinking without promoting the formation of covalent bonds in between. One of the polymers is hydrophobic and has good chemical, mechanical, and thermal properties, while the other is an ionic conductor. Main researches for membranes in this category are related with materials based on PVA, PPO, polyethylene, and polysulfone. They are easy to fabricate, and the range of polymers that can be used is wide. Additionally, they exhibit low electrical resistance and high mechanical strength, chemical stability, durability, and can be produced at a reasonable cost. However, since the constituent materials are not covalently bonded, the conductive polymer slowly diffuses out of the membrane with time, which causes progressive losses of conductivity and ion exchange capacity. Furthermore, although these membranes can reach ionic conductivities

higher than heterogeneous membranes (2–5 mS/cm), they are still very low for their use in a fuel cell [3, 14].

### 2.3. Homogeneous membranes

They are polymers composed of one type of material that is modified to have ion exchange capacity. In these materials, the cationic functional groups (usually quaternary amines) are covalently attached to the polymer backbone to generate ionic sites with an associated mobile counterion [6, 28]. According to how they are functionalized, homogeneous membranes can be classified into:

#### 2.3.1. Copolymerization of monomers

Copolymerization is a process in which 2 or more monomers combine into a single polymeric chain. The most promising membranes produced by this method are based on chloromethylstyrene and divinylbenzene. However, they have as disadvantage the low availability of chloromethylstyrene and high cost of divinylbenzene [3, 28].

#### 2.3.2. Radiation grafting

These membranes are conformed by a hydrophobic polymer backbone to which cationic functional groups are grafted by irradiation, UV, or plasma methods [3]. As the most important materials in this category are the poly(fluorinated ethylene-propylene) (FEP) and poly(ethylene-co-tetrafluoroethylene) (ETFE) membranes, both functionalized with polyvinylbenzene (PVB) and trimethylammonium hydroxide groups. They have a very high ionic conductivity with respect to other types of membranes (between 10 and 45 mS/cm) and excellent mechanical properties. However, they are currently impractical for massive production because of the high cost of their constituent components (especially for fluorinated membrane) and the grafting processes [6, 20].

#### 2.3.3. Chemical modification

These membranes are the most researched due to they can reach high ionic conductivities at a lower fabrication cost than membranes produced by copolymerization and radiation grafting. However, chemical modification methods are difficult to control and reproduce. In consequence, the resulting quality of the membranes is highly dependent on the rigor of the fabrication procedure. Some of the anion-exchange membranes of this category are based on polystyrene, PVA, PVB, epichlorohydrin, polyethylene glycol, ethers, aromatic esters, guanidine, polysulfone, and polypropylene [3, 6].

Homogeneous membranes are to date the most efficient and promising electrolytes for AEMFCs because of their superior ionic conductivity and durability with respect to the other membrane categories. However, yet there is no a consolidated material that fulfills the conditions required to achieve an optimal operation in an AEMFC, despite the fact that significant advances have been made in the last years with respect to the quality of their fabrication and properties. For that reason, it is essential not only to improve them from the experimental



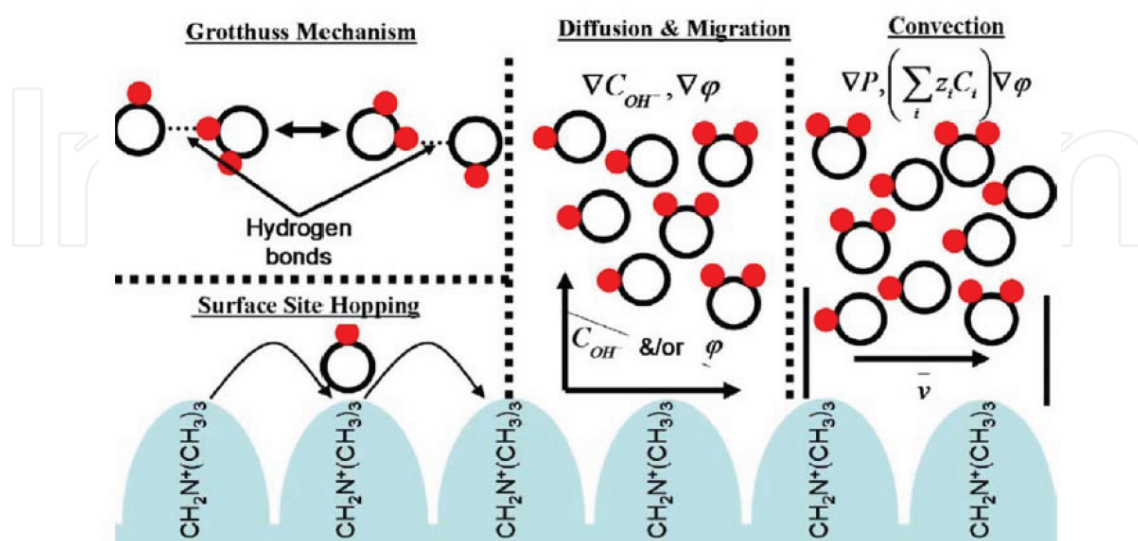
work, but also with theoretical studies to understand the characteristics of the transport mechanisms of hydroxide ions through anion-exchange membranes and how they influence their ionic conductivity and chemical stability as it is shown below.

### 3. Theoretical studies

As was introduced in previous sections, a good alternative to design efficient anion-exchange membranes is the implementation of theoretical models to identify, analyze, and complement the experimental findings about transport phenomena within them. However, studies of this type are few, and the characteristics of such transport phenomena are not well known and are still in discussion to date [29]. In order to identify them, studies for transport of hydronium ions ( $\text{H}_3\text{O}^+$ ) in hydrated proton-exchange membranes have been taken as a starting point under the premise that the characteristics of ionic transport for both anionic and protonic membranes could be similar (which is not strictly true) [30, 31]. Thus, in **Figure 3** are schematically shown the main transport mechanisms for hydroxide ions through anion-exchange membranes that have been proposed in the literature. These include diffusion, which consist of molecular or *en masse* diffusion, structural diffusion or Grotthuss mechanism and surface site hopping; migration and convection.

#### 3.1. Diffusion

It is defined as the transport of molecules due to a chemical potential gradient of one or more components in the absence of an electric field [32]. Within a hydrated anion-exchange membrane, hydroxide ions can diffuse by three modalities: the traditional *en masse* diffusion, Grotthuss mechanism, and surface site hopping. The first two mechanisms take place at the

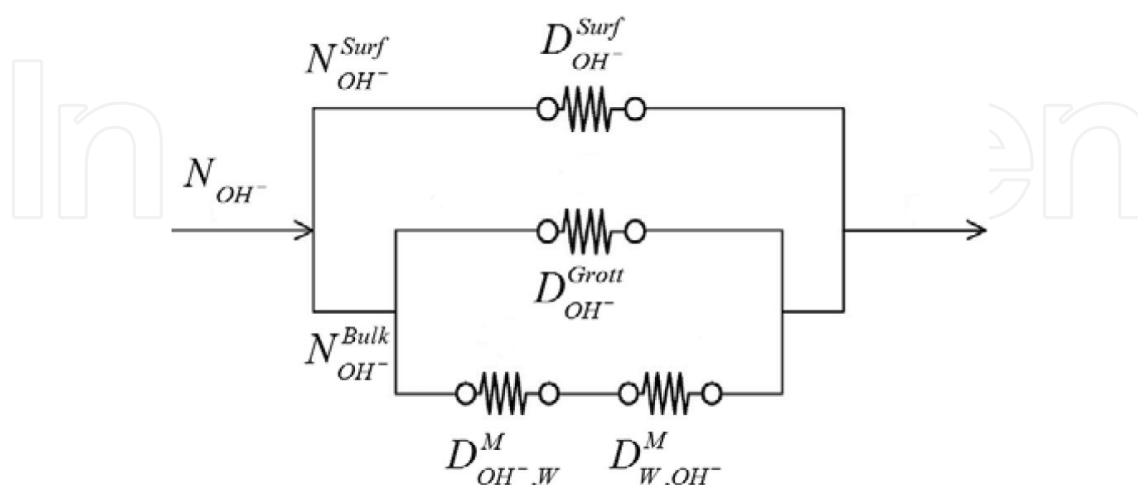


**Figure 3.** Transport mechanisms proposed for hydroxide ions in anion-exchange membranes. Reprinted with permission from *J. Electrochem. Soc.*, 2010; 157(3): B327. Copyright 2010, The Electrochemical Society.

bulk of water molecules (usually in the middle region of the membrane pores and far from its backbone and side chains), while the latter takes place on the surface of the polymer cationic functional chains [33]. A visualization of the way hydroxide ions can diffuse by these mechanisms is depicted as an electric circuit in **Figure 4**.

In which  $N_{OH^-}$  is the total flux of hydroxide ions transported through the membrane,  $N_{OH^-}^{Surf}$  is the flux of hydroxide ions transported through the surface of the polymer chains and  $N_{OH^-}^{Bulk}$  is the flux of hydroxide ions transported through the region of bulk water. Additionally,  $D_{OH^-}^{Surf}$  and  $D_{OH^-}^{Grott}$  are the contributions to total diffusion coefficient from surface site hopping and Grotthuss mechanisms, while  $D_{OH^-,W}^M$  and  $D_{W,OH^-}^M$  are respectively the contributions from *en masse* diffusion of hydroxide ions and water molecules.

Contributions of each mechanism to total diffusion are strongly influenced by the nanostructure and water content of the anion-exchange membrane [33, 34]. On the one hand, at low hydration levels, pores of the polymer are narrow and cationic side chains are very close to each other. In consequence, solvation of water molecules and interaction between them and hydroxide ions via hydrogen bonding are very low with respect to the electrostatic forces exerted by the cationic chains on the latters. Therefore, transport of hydroxide ions is more likely to take place on the surface of the polymeric chains by surface site hopping and molecular diffusion at low rates. In addition, ionic conductivity of the anion-exchange membrane will be very low. On the other hand, at high hydration levels, the pores of the polymer swell and give place to wide continuous channels where regions of bulk water can be formed. Cationic functional chains will be more separated, thus their influence on hydroxide ions is reduced and dissociation from solvation of water molecules will be more likely. Therefore, transport of hydroxide ions takes place mostly by charge defect transfer (Grotthuss mechanism) in the bulk water region at high rates: the ionic conductivity of the anion-exchange membrane under that condition will reach its highest values [34].



**Figure 4.** Electric circuit analogy of the transport mechanisms by which hydroxide ions can diffuse through anion exchange membranes. Reprinted with permission from *J. Electrochem. Soc.*, 2005; 152(3): E123. Copyright 2005, The Electrochemical Society.



In order to gain deeper understanding of the mentioned diffusion mechanisms, a general description for each one and their implementation in mathematical models is given in the next subsections.

### 3.1.1. *en masse diffusion*

The molecular movement of hydroxide ions due to concentration (or activity) gradients can be described according to Fick's law:

$$N_{OH^-}^M = -D_{OH^-,W}^M \nabla c_{OH^-} \quad (4)$$

in which  $N_{OH^-}^M$  is the flux of hydroxide ions due to *en masse* diffusion and  $c_{OH^-}$  their corresponding concentration. However, since water molecules are also diffusing by their own gradient and there are also frictional interactions with the membrane, it is more rigorous to use the multicomponent Stefan-Maxwell equation to take into account those effects in the mass diffusion of hydroxide ions [29, 32]:

$$\nabla x_i = \sum_{j \neq i}^n \frac{x_i N_j - x_j N_i}{c_T D_{i,j}^M} - \frac{N_i}{c_T D_{i,AEM}^M} \quad (5)$$

in which  $x_i$  is the mole fraction of specie  $i$ ,  $c_T$  the total concentration of all species,  $D_{i,j}^M$  the mass diffusion coefficient between species  $i$  and  $j$  and  $D_{i,AEM}^M$  the mass diffusion coefficient between specie  $i$  and the membrane structure. Expressing Eq. (5) for hydroxide ions in a hydrated membrane, it becomes:

$$\nabla x_{OH^-} = \frac{x_{OH^-} N_W - x_W N_{OH^-}}{c_T D_{OH^-,W}^M} - \frac{N_{OH^-}}{c_T D_{OH^-,AEM}^M} \quad (6)$$

The first term of the right side of Eq. (6) corresponds to the interactions between water molecules and hydroxide ions and the other represents the frictional effects of the membrane. In addition, to account for Knudsen diffusion, binary diffusion coefficients can be expressed as a parallel resistance with the following form [32]:

$$D_{i,j}^{M,eff} = \frac{1}{\frac{1}{D_{i,j}^M} + \frac{1}{D_{Ki}}} \quad (7)$$

The Knudsen diffusion coefficient ( $D_{Ki}$ ) can be approximated from the kinetic theory of gases [32]:

$$D_{Ki} = \frac{d}{3} \sqrt{\frac{8RT}{\pi M_i}} \quad (8)$$

in which  $d$  is the pore diameter of the membrane,  $R$  the ideal gas constant,  $T$  the temperature, and  $M_i$  the molecular weight of specie  $i$ . Alternatively, effective diffusion coefficient of Eq. (7) can be expressed in terms of porosity ( $\epsilon$ ) and tortuosity ( $\tau$ ) by the following relation [35]:

$$D_{i,j}^{M,eff} = \frac{\varepsilon}{\tau} D_{i,j}^M \quad (9)$$

or by using the Bruggeman percolation model, initially used for hydronium ions in proton-exchange membranes but later extended to hydroxide ions in anion-exchange membranes [29]:

$$D_{i,j}^{M,eff} = (v_w - v_{w,o})^q D_{i,j}^M \quad (10)$$

in which  $v_w$  is the volume fraction in the membrane,  $v_{w,o}$  the volume fraction of water at percolation limit (minimum water content required to allow transport of hydroxide ions through the membrane) and  $q$  the Bruggeman constant.

Binary diffusion coefficients ( $D_{i,j}^M$  and  $D_{i,AEM}^M$ ) must be obtained either from experimental measurements or empirical correlations. By including effective diffusion coefficients in Eq. (6), it gets the following form:

$$\nabla x_{OH^-} = \frac{x_{OH^-} N_W - x_W N_{OH^-}}{c_T D_{OH^-,W}^{M,eff}} - \frac{N_{OH^-}}{c_T D_{OH^-,AEM}^{M,eff}} \quad (11)$$

In order to obtain the flux and mole fraction profiles for hydroxide ions from Eq. (11), it must be solved simultaneously with the Stefan-Maxwell equation for water:

$$\nabla x_W = \frac{x_W N_{OH^-} - x_{OH^-} N_W}{c_T D_{W,OH^-}^{M,eff}} - \frac{N_W}{c_T D_{W,AEM}^{M,eff}} \quad (12)$$

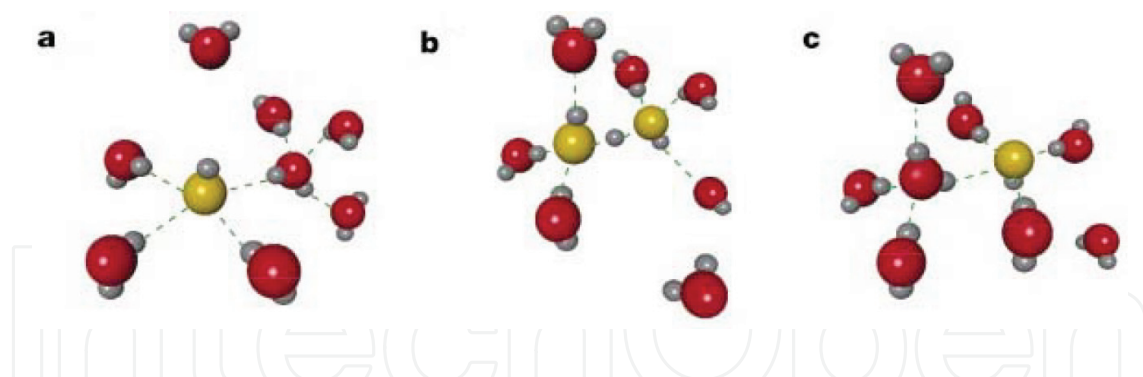
In addition, appropriate boundary conditions must be established. These can be obtained by coupling the transport model of Eqs. (11) and (12) with a global model for the AEMFC.

### 3.1.2. Grotthuss mechanism

Also known as structural diffusion and proton hopping, it is a transport mechanism by which a protonic excess (hydronium ( $H_3O^+$ ) for instance) or defect (hydroxide ( $OH^-$ ) for instance) of an ionic specie diffuses through the hydrogen bond network of water molecules by means of a reactive process caused by fluctuations in the coordination bonds between ions and water that involve the formation and cleavage of hydrogen bonds [36–39].

Currently, the exact description of Grotthuss mechanism for hydroxide ions is still in discussion, and different theories have been proposed. Among them, the dynamic hypercoordination theory is considered the most accurate description to date. However, it is postulated for pure aqueous medium and has not been extended to consider the presence of an anion-exchange membrane.

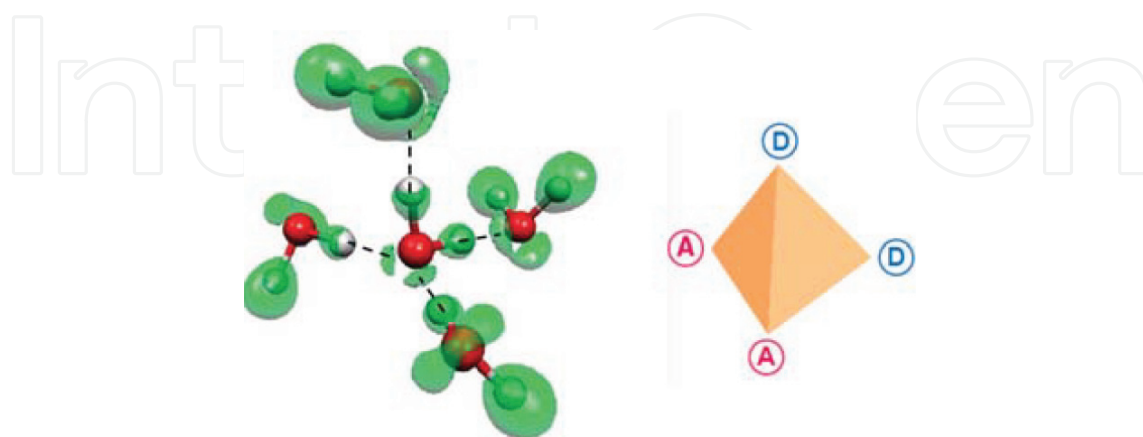
The steps involved in the Grotthuss mechanism according to dynamic hypercoordination theory are shown in **Figure 5**. It is based on the presolvation concept, which establishes that species with charge defects must be first solvated by water molecules to perform the charge defect transfer [38, 40]. For just water, its molecules form tetrahedral hypercoordinated complexes with adjacent



**Figure 5.** Grotthuss mechanism for hydroxide ions in pure water is according to the dynamic hypercoordination theory. Colors code: oxygen of water molecules is in red, oxygen of molecules with charge defects is in yellow, and hydrogen is in gray. Reprinted by permission from Springer Customer Service Centre GmbH: Springer Nature, The nature and transport mechanism of hydrated hydroxide ions in aqueous solution, M.E. Tuckerman, D. Marx, Copyright 2002.

molecules by donating and receiving two hydrogen bonds, respectively [41, 42] as shown in **Figure 6**. According to the hypercoordination theory, when a hydroxide ion goes into the water network, it adopts a square-planar topology (**Figure 5a**) in which its oxygen atom accepts four hydrogen bonds from neighboring water molecules (forming the anion  $\text{H}_9\text{O}_5^-$ ). In addition, the hydrogen atom of the hydroxide ion is delocalized around the oxygen atom and stays without establishing coordination bonds. To carry out the charge defect transfer, hydroxide ion must first reduce its coordination number by breaking one of the hydrogen bonds received from a water molecule and then establishing bonding between its hydrogen atom and another nearby water molecule. This allows the ion to take the topology of a fully coordinated water molecule, promoting the transfer of the anionic defect to an adjacent molecule in a process in which the complex  $\text{H}_3\text{O}_2^-$  is temporarily formed (**Figure 5b**). When the transfer is finished, the receiving molecule rearranges to take the preferential square-planar configuration of a hydroxide ion, thereby completing the transport process (**Figure 5c**) [36–38, 40].

It is considered that Grotthuss mechanism has a predominant contribution to hydroxide mobility through hydrated membranes according to: (a) experimental studies about hydroxide mobility in pure aqueous medium [43, 44], (b) theoretical studies about hydroxide mobility in



**Figure 6.** Left: connectivity of a water molecule with four adjacent water molecules. Electronic clouds are indicated in green. Right: tetrahedral representation of the water molecule indicating the donated (D) and accepted (A) hydrogen bonds. From D. Marx: Throwing Tetrahedral Dice. Science. 2004; 303: 634–636. Reprinted with permission from AAAS.

pure aqueous medium with *ab initio* Molecular Dynamics (AIMD) [37, 38], and (c) analogous studies for PEMFCs [33, 45–48].

### 3.1.3. Surface site hopping

It involves the movement of hydroxide ions by means of successive hops from one side chain of the membrane to another due to strong electrostatic attractive forces exerted by the cationic functional groups on the ions [3, 29, 33]. This process takes place as follows: first, a hydroxide ion attached to a cationic functional group is solvated and dissociated by water molecules. After that, an adjacent side chain attracts the solvated ion to its surface, then the process repeats. This results in a net displacement of the hydroxide ion through the membrane equal to the distance between the two cationic side chains.

Although this mechanism is more likely at low water contents of the membrane, it is considered a secondary process because of the strong interactions between water molecules in the system and the hydrophilic cationic functional groups, which act as a barrier for the hydroxide ions to interact and reach the surface of the latter. This reduces the possibility of this mechanism to take place over the others [29].

Both Grotthuss mechanism and surface site hopping take place at atomic length and time scale and can only be effectively studied through quantum physic techniques like AIMD because of the nature of this phenomenon. At the macroscale, their contributions to total diffusion in mathematical models can be accounted in following way: Grotthuss mechanism, which takes place at the bulk of water molecules, can be accounted by extending the expression for the effective mass diffusion of hydroxide ions in water (Eq. (7)) as:

$$D_{OH^-,W}^{eff} = \frac{1}{\frac{1}{D_{OH^-,W}^{M,eff}} + \frac{1}{D_{OH^-}^{Grott}}} \quad (13)$$

Surface site hopping can be accounted by applying empirical corrections to the influence of the membrane structure on hydroxide mobility (that is  $D_{OH^-,AEM}^{M,eff}$ ) to include not only frictional effects but also surface phenomena [29]. By applying Eq. (13) and an appropriate correction to  $D_{OH^-,AEM}^{M,eff}$  into Eq. (11), one gets:

$$\nabla x_{OH^-} = \frac{x_{OH^-} N_W - x_W N_{OH^-}}{c_T D_{OH^-,W}^{eff}} - \frac{N_{OH^-}}{c_T D_{OH^-,AEM}^{eff}} \quad (14)$$

in which  $D_{OH^-,AEM}^{eff}$  is the effective diffusion coefficient between hydroxide ions and membrane that accounts for surface site hopping. Eq. (14) combined with Eq. (13) are rigorous expressions that take into account all the diffusive phenomena that hydroxide ions can undergo. However, its full application is very limited because Grotthuss mechanism and surface site hopping have not been formally characterized for anion-exchange membranes, and thus, there are no accurate correlations to represent them (i.e., expressions for  $D_{OH^-}^{Grott}$  to account for Grotthuss mechanism and either  $D_{OH^-,AEM}^{eff}$  or  $D_{OH^-}^{Surf}$  in **Figure 4** to account for surface site hopping) like for

proton-exchange membranes (see for instance, the research of Choi et al. [33]). For that reason, current transport models approximate  $D_{OH^-,W}^{eff}$  by combining the value of the binary diffusion coefficient of hydroxide ions in pure liquid water at 25°C ( $5.3 \times 10^{-9} \text{ m}^2/\text{s}$ ) with empirical correlations to take into account effects of temperature, pressure and water content, which in practice works well to obtain accurate solutions to the transport models but screening how exactly diffusion of hydroxide ions is taking place and how it changes with temperature, pressure, and water content.

### 3.2. Convection

Convective transport can take place mainly due to a pressure gradient between the boundaries of the anode and cathode diffusion layers of the fuel cell and the membrane. It is also due to electro-osmotic drag, in which a flux of water molecules is induced by the motion of hydroxide ions in the absence of concentration gradients (i.e., by electric potential gradients) [3, 20, 29].

In electrochemical systems, a convection velocity can be defined by means of the Schoegel's equation [29]:

$$v_{conv} = \frac{B_o}{\eta} \left[ \nabla P + \left( \sum_i^n z_i c_i \right) F \nabla \phi \right] \quad (15)$$

in which  $B_o$  is the d'arcy hydraulic permeability,  $\eta$  the dynamic viscosity,  $F$  the Faraday constant,  $z_i$  the charge number of specie  $i$  and  $\phi$  the electric potential. The terms in the brackets at right side of Eq. (15) are respectively the contributions to convection by pressure gradients and electro-osmotic drag. It is important to point out that Schoegel's equation assumes that charged species in the radial direction of the membrane pores are uniformly distributed, thus potential gradients are neglected. This is indeed the case for exchange membranes in which pore sizes are small so there are not considerable localized variations in the radial direction [29].

If transport by convection and diffusion are taking place simultaneously, Eq. (15) can be combined with Eq. (5):

$$\nabla x_i = \sum_{j \neq i}^n \frac{x_i N_j - x_j N_i}{c_T D_{i,j}^{eff}} - \frac{N_i}{c_T D_{i,AEM}^{eff}} - \frac{B_o}{\eta D_{i,AEM}^{eff}} \left[ \nabla P + \left( \sum_i^n z_i c_i \right) F \nabla \phi \right] \quad (16)$$

in which binary diffusion coefficient was replaced by effective diffusion coefficients to include the effect of membrane structure and all the possible diffusion mechanisms affecting specie  $i$  (as was described in Section 3.1). In addition, convection term appears divided by  $D_{i,AEM}^{eff}$  to take into account any frictional effect of the membrane on this mechanism. Applying the abovementioned definitions into Eqs. (11) and (12), the following set of equations is obtained:



$$\nabla x_{OH^-} = \frac{x_{OH^-}N_W - x_WN_{OH^-}}{c_TD_{OH^-,W}^{eff}} - \frac{N_{OH^-}}{c_TD_{OH^-,AEM}^{eff}} - \frac{B_o}{\eta D_{OH^-,AEM}^{eff}} [\nabla P + c_{OH^-}F\nabla\phi] \quad (17)$$

$$\nabla x_W = \frac{x_WN_{OH^-} - x_{OH^-}N_W}{c_TD_{W,OH^-}^{M,eff}} - \frac{N_W}{c_TD_{W,AEM}^{M,eff}} - \frac{B_o}{\eta D_{W,AEM}^{M,eff}} [\nabla P + c_{OH^-}F\nabla\phi] \quad (18)$$

Transport by convection is especially important at high hydration levels in which porous structure of the membrane swells enough to give place to continuous channels that connect the anode with cathode, so an effective pressure gradient can be established. In addition, convection by electro-osmotic drag must be considered at high concentrations of hydroxide ions when electric potential gradients could be significant.

### 3.3. Migration

It is defined as the motion of charged species due to electric potential gradients resulting from the electrostatic interactions between them. Transport by migration can be described according to Ohm's law:

$$i = -\sigma\nabla\phi \quad (19)$$

in which  $\sigma$  is the ionic conductivity of the membrane,  $\phi$  the electric potential and  $i$  the current density. The latter can be related to molar flux by the following definition:

$$i = F \sum_i^n z_i N_i \quad (20)$$

When either diffusion or convection takes place simultaneously with migration, the generalized Stefan-Maxwell equations (GSME) for a system of  $n$ -particles can be used [29]:

$$\frac{c_i}{RT} \nabla \tilde{\mu}_i = \sum_{j \neq i}^n \frac{x_i N_j - x_j N_i}{D_{i,j}^{eff}} - \frac{N_i}{D_{i,AEM}^{eff}} - \frac{B_o c_i}{\eta D_{i,AEM}^{eff}} \left[ \nabla P + \left( \sum_i^n z_i c_i \right) F \nabla \phi \right] \quad (21)$$

which is analogous to Eq. (16) but expressed in terms of electrochemical potential gradients:

$$\nabla \tilde{\mu}_i = \nabla \mu_i + z_i F \nabla \phi \quad (22)$$

Alternatively, the dilute-solution or concentrate-solution approaches can be applied. In the dilute-solution approximation, interactions between solute molecules are neglected, and the Nernst-Planck equation can be used [32]:

$$N_i = -z_i u_i F c_i \nabla \phi - D_i \nabla c_i + c_i v_{conv} \quad (23)$$

in which  $u_i$  is the mobility of specie  $i$ . The terms of the right correspond respectively to migration, diffusion, and convection (in which electro-osmotic drag is neglected). In addition, the Nernst-Einstein equation can be used to relate ionic mobility (and conductivity) with diffusivity and reduce the number of transport properties in Eq. (23) [32]:

$$D_i = RTu_i \quad (24)$$

However, Eqs. (23) and (24) apply rigorously just at infinite dilution ( $<0.01 \text{ mol/dm}^3$  [49]), which most of the time is not the case for a membrane in an AEMFC. Therefore, concentrated-solution theory is preferred if enough information about the required parameters and transport properties is available [32]. Under this approach, the following set of equations for hydroxide ions and water can be obtained (see detailed derivation in Refs. [50, 51]):

$$i_{OH^-} = -\sigma \nabla \phi_{OH^-} - \frac{\sigma \xi}{F} \nabla \mu_w \quad (25)$$

$$N_w = -\frac{\sigma \xi}{F} \nabla \phi_{OH^-} - \left( \alpha + \frac{\sigma \xi^2}{F^2} \right) \nabla \mu_w \quad (26)$$

in which  $\xi$  is the electro-osmotic drag coefficient and  $\alpha$  is a transport coefficient that can be related either to a hydraulic pressure gradient or a concentration gradient through the definition of chemical potential [32]:

$$\nabla \mu_w = RT \nabla \ln a_w + \bar{V}_w \nabla P \quad (27)$$

in which  $a_w$  is the activity and  $\bar{V}_w$  the molar volume. Along with diffusion, transport by migration usually has a strong effect in the mobility of hydroxide ions even at low ionic concentrations. Therefore, application of concentrated-solution theory could be considered essential for the correct description of full transport phenomena of hydroxide ions. However, lack of information about most of the transport properties and parameters in the model for anion-exchange membranes limits greatly its use. Therefore, mathematical expressions for those properties in anion-exchange membranes are based on correlations fully characterized and validated for proton-exchange membranes [29], on the basis that transport phenomena in both systems should be equivalent as was mentioned at the beginning of this section.

#### 4. Conclusions, challenges, and future work

Although PEMFCs are nowadays the main and most attractive fuel cell technology for mobile applications, AEMFCs have significant advantages over PEMFCs that give them a greater potential for massive production at low cost: (a) the oxygen reduction reaction is more favorable in alkaline medium. Therefore, catalysts as silver or nickel, which are less expensive than platinum (predominantly used in PEMFCs and their major drawback) can be used [52]. (b) Corrosion problems are reduced because metals and coal generally used in bipolar plates, current collectors and catalysts are chemically more stable in alkaline than in acid medium.

This allows the use of less expensive components such as current collectors of nickel and thin metal bipolar plates [8]. (c) The oxidation of alcohols such as methanol and ethanol is more favorable in alkaline medium. This allows a more efficient alcohol oxidation, and the amount of platinum and ruthenium in catalysts can be reduced [53]. However, more intensive research is required.

Homogeneous membranes are currently the most efficient electrolytes for AEMFCs because of their high ionic conductivity and durability in comparison with heterogeneous membranes and interpenetrated polymer networks. However, they have strong drawbacks that need to be overcome. Membranes produced by copolymerization using chloromethylstyrene and divinylbenzene as their base materials have shown both high ionic conductivities and chemical stability at fuel cell conditions, but as was mentioned in Section 2, they are impractical because of the low availability of chloromethylstyrene and high cost of divinylbenzene. Conductive polymers functionalized by radiation grafting procedures have been extensively researched and have the highest ionic conductivities among the listed membrane types. In fact, most of the commercial membranes nowadays belong to this category. However, as membranes produced by copolymerization, they are very expensive and unfeasible for a large-scale production. Finally, homogeneous membranes functionalized by chemical modification can be produced at low cost and be as conductive and efficient as membranes produced by copolymerization and radiation grafting. Therefore, they are the most promising materials for a future mass production of AEMFCs. The main problem with these materials is the attachment process of the cationic functional groups and their chemical stability. First, fabrication procedures need to be improved and standardized so they can be effectively implement at large-scale production. Second, membranes of this category use trimethylammonium-based chains as the cationic functional groups, which are very reactive with hydroxide ions. In consequence, they have poor stability at operational conditions of the fuel cell and tend to degrade at early operation times.

Theoretical understanding of the transport mechanisms taking place within anion-exchange membranes is a straightforward way to design effective procedures to fabricate anion-exchange membranes with the required characteristics to operate efficiently and stably at the conditions of an AEMFC. Unfortunately, there are a lot of conceptual gaps and lack of information that currently limits strongly this possibility. It is required a better understanding and particularization of the transport theories behind those models to anion-exchange membranes. For instance, great part of the transport properties and parameters required by the most rigorous models (like GSME and concentrated-solution theory) have not been experimentally measured or mathematically defined for anion-exchange membranes, so they still are calculated from correlations and theories extensively studied and validated for proton-exchange membranes regardless their application could not be correct for alkaline medium. Moreover, the characteristics of some of the transport mechanisms involved in the mobility of hydroxide ions are not exactly known. This is, for example, the case of the mechanism considered to have the major contribution to the hydroxide mobility through hydrated anion-exchange membranes, that is, Grotthuss mechanism. Mobility studies for hydroxide ions in pure aqueous medium have approached the basic characteristics of the mechanism, but it has not been done yet an extension of those studies to anion-exchange membranes to take into account key

aspects that could affect dramatically its development such as: (a) water content of the conductive polymer, which affects its morphology and distribution of its cationic functional groups and (b) the type of cationic functional group, which is responsible of the electrostatic forces exerted on the hydroxide ions and water, steric and frictional effects due to the structure and size of the cationic group and the electrical double layer effects due to the surface distribution of electrostatically attracted molecules [14, 33, 34, 45].

All the above mentioned approaches are nowadays active research areas of high interest. If successful alternatives to improve the current limitations of the existent polymeric systems could be obtained from the co-development of experimental and theoretical studies, AEMFCs could not only exceed in efficiency and economy the PEMFCs, but also become a competitive, feasible, and sustainable technology to other alternative power generation sources especially for portable and stationary applications at low temperature.

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