Water Transport in Polyelectrolyte Fuel Cells

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Abstract: In this review, previous researches related to water transport in PEMFC are comprehensively reviewed. The state and transport mechanism of water in different components are elaborated in detail. The water transport in anion exchange membrane fuel cell (AEMFC) and the novel bipolar membrane fuel cell (BPMFC) are also discussed based on the cases in PEMFC. The water transport mechanism in AEMFC and BPMFC are similar to that of PEMFC, while the water management would be much difficult since the limitation properties of anion exchange membrane. In another hand, the difference between electrode reactions and membrane interface reactions for BPMFC make the transport of water more complicated. Fully understand the water transport in membrane electrode assembly is important in the develop of novel self-humidification fuel cells. As a result, the attractive cell configuration of BPMFC would make it a potential candidate for smart self-humidification fuel cells.

1. Introduction
Fuel cell is a kind of energy transition device that transforms the chemical energy saved in the fuel and oxidant to electric energy with the electrochemical reaction. Fuel cells involve various varieties, which are classified according to the differences of electrolytes. For example, there are Alkaline Fuel Cell (AFC), Polymer Electrolyte Fuel Cell, (PEFC), Phosphoric Acid Fuel Cell, (PAFC), Molten Carbonate Fuel Cell (MCFC) and Solid Oxide Fuel Cell (SOFC). Different types of fuel cells have respective application scopes. For example, PAFC, MCFC and SOFC are applicable for fixed power stations, but PEFC, AFC, etc can be applied for the mobile power of vehicles or portable devices. Because of the advantages of low work temperature, high power density, low-temperature start-up and zero/low exhal, PEFC is also called as Proton Exchange Membrane Fuel Cell (PEMFC), which has been developed to be the most anticipated dynamic power applied for vehicles and back-up power stations. On the basis of settling the precedents’ experiments and model research results, this paper elaborates different water transport mechanism of PEFCs, including mature, hot-spot anion exchange membrane, anion exchange membrane fuel cell (AEMFC) and new Bipolar Membrane Fuel Cell (BPMFC), summarizes the similarities and differences of its water management strategies, so as to explore water/ion/electron transport mechanism in the fuel battery interface in a better way.

2. Anion exchange membrane fuel cell
In recent years, with the long-term development of anion exchange membrane research, anion exchange membrane fuel cell (AEMFC) has gradually been extensively focused on. In AEMFC, the carbonation problem in front of traditional anion battery can be buffered, but the electron-chemical reaction dynamics brought by the anion environment is faster than the acid environment, which can satisfy the
application requirement of non-noble metal catalyst. Therefore, AEMFC can rapidly develop by its unique advantages.

2.1. Anion exchange membrane fuel cell work mechanism

![Anion exchange membrane fuel cell electrode figure](image)

Figure 1 is AEMFC hydrogen mono-cell membrane figure, consisting of anion positive electrode, anion cathode electrode and anion exchange membrane between two electrodes. Through the gas diffusion layer, leveling layer, oxygen arrives the catalytic layer and reacts with electrons, water in the anion catalyst layer to form caustic anion. Caustic anion exchange membrane is transported to the positive catalyst layer, reacting with the hydrogen from the positive flow field to generate water.

Positive half reaction:

\[
\text{H}_2 + 2\text{OH}^- \rightarrow 2\text{H}_2\text{O} + 2\text{e}^- \quad E_A^0 = -0.83 \text{V vs. SHE} 
\]  

(2.1)

Positive half reaction:

\[
\frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^- \quad E_C^0 = 0.40 \text{V vs. SHE} 
\]  

(2.2)

Battery total reaction:

\[
\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O} \quad E_{\text{cell}}^0 = 1.23 \text{V} 
\]  

(2.3)

In the same, \(E_A^0, E_C^0\) are standard balanced potential of anode and cathode to the standard hydrogen electrode, \(E_{\text{cell}}^0\) is the standard reversible balanced voltage of the battery.

Different from PEMFC, water reacts in the anode catalyst layer in AEMFC, and water is the reactant in the cathode half reaction. That is to say, without the proper water management strategy, water distribution will be more uneven in AEMFC.

Under normal working conditions, water exists in the pore of gas diffusion layer in the form of gas-liquid two-state, and the phase transformation reaction of condensation and evaporation is controlled by local vapor pressure environment. Gas diffusion layer not only provides the transmission channel of reaction gas to catalytic layer, but also transmits the water produced by reaction and the electrons needed for reaction, and even heat transfer. Usually for carbon paper or carbon cloth and other porous carbon materials. Carbon cloth is as soft as textiles, while carbon paper is quite fragile due to its thermosetting resin. The flexibility of another carbon felt material is between carbon cloth and carbon paper. The spatial homogeneity and anisotropy of these materials are different. Because these materials are made of hydrophilic carbon fibers, hydrophobic treatment with PTFE is usually non-uniform to facilitate more efficient drainage. Therefore, the internal pore structure of gas diffusion layer materials will have
different hydrophobic and hydrophobic properties depending on the amount of PTFE added, forming hydrophobic pore, hydrophilic pore and even mixed hydrophobic pore.

2.2. Anion exchange membrane

Anion exchange membrane or polymer contains positive ion functional groups, so it can conduct negative ions, such as $\text{OH}^-$ and $\text{Cl}^-$. These cationic groups can connect with the extended lateral chain or directly with the main chain. The common main chains include: polyaromatic ethers such as polysulfone, polyether ketone, polyether imide, polyether diazole, polyphenylene ether, polyphenylene, perfluorine, polybenzimidazole, polyepichlorohydrin, unsaturated polypropylene, polyethylene, etc. Positive ion functional groups with more research include quaternary ammonium, heterocyclic, guanidine salt, $p$-based functional group, sulfonium salt, metal ion system, etc.

In order to ensure the high-efficient, stable and long-duration operation of fuel cell, anion exchange membrane must satisfy the following conditions: able to form the flexible and compact thin film, separate from fuels and oxidants; high ionic electronic conductivity, no lower than 10 mS cm at the room temperature. At the battery working temperature, it should reach 100 mS cm as much as possible; due to its excellent chemical properties, heat and size stability, it should maintain the lowest swelling degree in the fuel cell’s working condition (for example, no higher than 30% at 80ºC). Obvious degradation is not caused; excellent mechanical strength (for example, mechanical tensile strength is no lower than 10 MPa at the room temperature); equipped with certain soluble property, able to form anion polymer solution in the specific solvent, used to prepare for membrane electrode catalyst layer.

It is commonly believed that two major defects of anion exchange membrane are as follow: it is badly stable at the status of $\text{OH}^-$, particularly in the environment of water shortage; another disadvantage is that $\text{OH}^-$’s electrical conductivity is much lower than the proton’s electrical conductivity in the acid ion’s exchange membrane. In the same, it is more significant in the environment of water shortage. Therefore, a lot of researchers are striving to developing anion exchange membrane material that satisfies the working needs of fuel cell at present. In the past few years, commercialized anion exchange membrane studied and developed by Japan Tokuyama Co., Ltd has attributed to the long-term development of AEMFC in output performance and stability, but it is still far from the level of PEMFC. Tokuyama A201 can be said as the anion exchange membrane closest to most comprehensive and commercial one at the current stage. Table 2 lists the basic properties of A201 and A901 anion exchange membrane studied and developed by Tokuyama Company.

Table 1. Basic properties of Tokuyama anion exchange membrane

| Property                        | A201 | A901 |
|---------------------------------|------|------|
| Thickness (μm)                  | 28   | 10   |
| Ion-exchange capacity (mol kg)  | 1.7  | 1.7  |
| Water content                   | 0.25 | 0.15 |
| OH conductance (S m)            | 1.14 | 2.9  |
| OH conductivity (S m)           | 4.2  | 3.8  |
| Burst strength (MPa)            | 0.4  | 0.2  |
| Dimensional change (wet to dry)|     |      |
| MD (%)                          | 2    | 1    |
| TD (%)                          | 6    | 4    |

23°C, 90% RH, facial electrical conductivity is obtained by two-electrode method in the hydrogen atmosphere.

2.3. Anion exchange membrane’s water transportation mechanism

Li, etc assessed the variations of A201’s water absorption and other temperature lines and water diffusion coefficients with the membrane’s water content at the temperature of 30ºC, 40ºC and 60ºC. Duan, etc water absorption and other temperature lines and ion’s electrical conductivity with the membrane’s water content at the temperature of 50ºC and 80ºC, and expressed that the real electrical
conductivity rate of A201 membrane is much lower than the result published by Tokuyama Company. The possible reason is that the membrane is contaminated by the carbon dioxide due to its exposure in the air, and CO$_3^{2-}$’s electrical conductivity rate is far lower than that of OH$^-$’s electrical conductivity rate.

According to the results assessed by the precedents, Jiao, etc obtained the relations between A201’s stable water contents and temperature and gas’s relative humidity though interpolation correction:

$$\lambda = (-0.605a^3 + 0.85a^2 - 0.205a + 0.153) \times (T - 313.15) + 39a^3 - 47.7a^2 + 23.4a + 0.117 \quad (2.4)$$

And the changes of ion’s electrical conductivity with the water content are:

$$\sigma_{OH^-} = 0.1334 - 3.882 \times 10^4T + (0.01148T - 3.909)v - (0.06690T - 23.01)v^2$$

$$+ (0.1227T - 42.61)v^3 - (0.06021T - 21.8)v^4$$

$$v = 0.8118 - 2.296 \times 10^{-3}T + (5.815 \times 10^{-3}T - 2.005)\lambda - (2.977 \times 10^{-3}T - 1.046)\lambda^2$$

$$+ (4.825 \times 10^{-4}T - 0.1676)\lambda^3 - (3.179 \times 10^{-5}T - 0.01094)\lambda^4$$

$$+ (7.427 \times 10^{-7}T - 2.539 \times 10^{-4})\lambda^5$$

As well as the water’s diffusion coefficients within the membrane:

$$D_w = \begin{cases} 
(0.0051T - 1.444) \times 10^{-10} & 0 < \lambda < 14 \\
([-23.2404 + 4.513\lambda - 0.28926\lambda^2 + 0.006131\lambda^3] \times (T - 303.15) \\
-79.826 + 17.928\lambda - 1.3329\lambda^2 + 0.03337\lambda^3) \times 10^{-10} & 14 < \lambda < 19 
\end{cases} \quad (2.6)$$

At the same time, according to A201 membrane’s electrical migration coefficients assessed by Li and etc at the temperature of 30℃ and 40℃, after the linear simulation, obtained:

$$n_d = 1.340 + 0.183\lambda \quad (2.7)$$

It can be seen that A201 membrane’s water absorption rate is higher than that of Nafion membrane, and its electrical conductivity and water diffusion coefficient is far from Nafion membrane. In addition, A201’s electrical migration function is stronger than that in Nafion, which further leads to the bad water distribution situation in AEMFC. Therefore, in the latest anion exchange membrane development, researchers put forward designing the functional hydrophilic like Nafion membrane so as to form the microscopic separated structure within the membrane. In this case, in the scenario of low water absorption volume, it equips with higher electrical conductivity rate and size stability. Modifying the water transportation features of anion exchange membrane is the important means to buffer the water management difficulty in AEMFC radically.

Similar to the situation in Nafion membrane, the water flow in A201 can be divided as diffusion flow, electrical migration flow, pressure penetration flow, which are respectively expressed as:

$$J_{w,diff} = -D_w \nabla c_w = -\frac{P_{\text{mem}}}{E_w} D_w \nabla \lambda$$

$$J_{w,EOD} = -n_d \frac{i_{\text{ion}}}{F}$$

$$J_{w,hyd} = -c_w \frac{K_w}{\mu_w} \nabla p = -\lambda \frac{P_{\text{mem}}}{E_w} \frac{K_w}{\mu_w} \nabla p$$

The meaning of each symbol is consistent with that in the previous paper, and the only difference is that the direction of electrical migration current and OH$^-$ movement is all from the cathode to the anode.

2.4. Anion exchange membrane fuel cell’s water management research

Compared to PEMFC water management’s study, related study in AEMFC just begins. However, due to the consistent basic principles of the both, the experiences of PEMFC research can be extensively borrowed in AEMFC research. Therefore, a lot of reports on the experiments and simulated research of
AEMFC water management have also emerged in the recent years. Huo and etc established the numerical value model to analyze the water transportation process of AEMFC’s anode, and investigated the transportation of gas and liquid water in the gas diffusion layer and catalyst layer under different designing operation parameters. Results show that liquid water are significantly affected by the current density in the anode’s distribution, and its effects of the temperature on water is also obvious. However, the chemical equivalent has not caused big effects on the distribution of liquid water on the anode, and the influential trend of anode and cathode’s inlet humidity is similar to the anode’s liquid water contents. Deng, etc built a three-dimensional anode semi-battery transient model to study the dynamic characteristics while battery’s work status is changed. Research discovers that current density significantly affects the distribution of liquid water, and liquid water’s distribution is not sensitive to anode’s chemical equivalent. When current density lowers, it needs longer time to reach the stability. The similar scenario is that when the system’s temperature lowers, no obvious difference appears in the low-temperature interval. Jiao and etc built three-dimensional multi-phase non-equivalent-temperature AEMFC model and discovered that humidifying the anode can improve the cell’s performance, but it not significant at the high humidity level. Humidifying degree will change the water discharge mechanism; water is discharged in the form of the gas when it is partially humidified; and it is in the form of the liquid when it is completely humidified. Humidifying the cathode is more critical than the anode, for example, humidifying the cathode by the liquid water can improve the battery’s performance, particularly when the electricity is on in the high current density. When the cathode is humidified with the liquid water, water flows into the catalyst layer from the flow field instead of from the catalyst. Jiao believed that in order to balance the water contents of the anode and cathode, cathode’s liquid water humidification is quite necessary. In addition, reducing anion exchange membrane film’s thickness can promote water’s diffusion between the anode and cathode, lower the concentration polarization and modifies the battery’s performance. By analysing the model’s anion direct methanol fuel battery’s water management, Weinzierl and etc discovered that water replenishing is rather important in the high-current density, so water transportation within the membrane can be the restricted factor of battery’s performance possibly. Weinzierl and etc believed that while designing anion exchange membrane material, expect for electric conductivity and fuel penetration, membrane’s water transportation property appears to be rather important as well.

3. Bipolar membrane fuel cell
In summary of respective features of PEMFC and AEMFC, Lobyntseva and etc put forward the proposition of applying bipolar membrane into the development of new compound polar membrane fuel cell, and investigated the feasibility of the application of fuel cell consisting of DuPont Company’s Nafion membrane and FuMA-Tech Company’s fumapem series anion exchange membrane for Bipolar Membrane (BPM) in 2006. In 2014, Arges and etc investigated the feasibility of applying bipolar membrane electrodes into direct hydrazine battery, and attempted regarding silver catalyst as the anion catalyst of caustic battery. Ünlü and etc also put forward to the compound polar battery model by taking anion electrode as the electrode and acid exchange membrane as the separation film, and pointed out that its anode’s anion-acid (anion is close to the electrode) film interface reacts to consumes water, but anode’s half reaction produces water, but cathode half reaction consumes water, cathode side’s acid-anion (anion is close to the electrode) film interface reaction produces water. It makes the interface of consuming water close to that of producing water and the water distribution within the membrane electrode averaged, so as to reach the self-humidification effects of the battery. In the utilization of Nafion acid electrode, Nafion membrane and anion electrode prepared compound polar fuel cell, Ünlü and etc discovered that the higher the humidity of the reacted gas, the lower the battery performance becomes, and the electrode’s polar resistance increase, so as to presume that the model’s compound polar membrane fuel cell equips with the self-humidification function. However, the power output performance of bipolar membrane fuel cell reported by the current literature is still far from the optimal level of AEMFC, let alone the brilliant performance of PEMFC. The bipolar membrane fuel cell’s water transportation mechanism is still not specified. Therefore, it still needs large amounts of experiments.
and models to reveal the water transportation process and water management strategy of bipolar membrane fuel cell, so as to modify the battery’s performance and implement the favorable self-humidification control.

4. Conclusions
Polymer electrolyte fuel cell’s water transportation phenomenon has always been one of key points in the research. Research on the phenomenon and mechanism of proton exchange membrane fuel cell’s water transportation has been mature, which shows great enlightenment and reference function to the analysis and research of anion exchange membrane fuel cell’s water transportation that has rapidly risen in recent years. In the meantime, new bipolar membrane fuel cell summarizes the structural features of proton exchange membrane and anion exchange membrane, so it covers the water transportation’s features and phenomenon of proton exchange membrane fuel cell and anion exchange membrane fuel cell. However, because bipolar membrane fuel cell model breaks the singular membrane electrode structure of traditional polymer electrolyte fuel cell, making the position of water reaction interface and the types of electrode interface reaction can randomly collocate and form the unique water distribution characteristics. Therefore, studying its interface ions, water transportation mechanism will be beneficial to fully master and control the water management of the battery, so as to implement the self-humidification stable operation of the battery.

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