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A comprehensive review on water management strategies and developments in anion exchange membrane fuel cells

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Abstract

In spite of significant achievements in alkaline exchange membrane fuel cells (AEMFCs) in recent years, they are still lagging behind proton exchange membrane fuel cells (PEMFCs) due to performance instability. Among the relevant operational parameters of AEMFC, the researchers have found that poor water management within the cell was the main reason for failure of the system. In the past five years, numerous modeling and experimental works were reported proposing different strategies to improve water management of AEMFC. The achievable power output in AEMFCs is then comparable with that of PEMFCs or even more. Efforts have to be continued, but AEMFCs can become a strong competitor in the market place. This review paper discusses the strategies and developments impacting water management of AEMFCs providing knowledge source for upcoming studies.

Key words: AEMFC; Microporous layers; Gas diffusion layers; Ionomers; Electrocatalysts; Relative humidity.

Acronyms:

PEMFC:	Proton exchange membrane fuel cell
AFC:	Alkaline fuel cell
AEM:	Anion exchange membrane
AEMFC:	Anion exchange membrane fuel cell
HOR:	Hydrogen oxidation reaction
ORR:	Oxygen reduction reaction
GDL:	Gas diffusion layer
MPL:	Micro porous layer
PTFE:	Polytetrafluoroethylene
MEA:	Membrane electrode assembly
CL:	Catalyst layers
CCL:	Cathode catalyst layer
ACL:	Anode catalyst layer
CDL:	Cathode diffusion layer
CMPL:	Cathode micro porous layer
AMPL:	Anode micro porous layer
AEI:	Anion exchange ionomer
QA:	Quaternary ammonium
TMBA:	Trimethylbenzyl ammonium bromide
TEBA:	Triethylbenzyl ammonium chloride
IES:	Ion exchange sites
RH:	Relative humidity
VBTAC:	Vinyl benzyl trimethyl ammonium chloride
MAPTAC:	3-methacryloylamino propyl trimethylammonium chloride
DOE:	Department of energy
ETFE:	Ethylene-co-tetrafluoroethylene

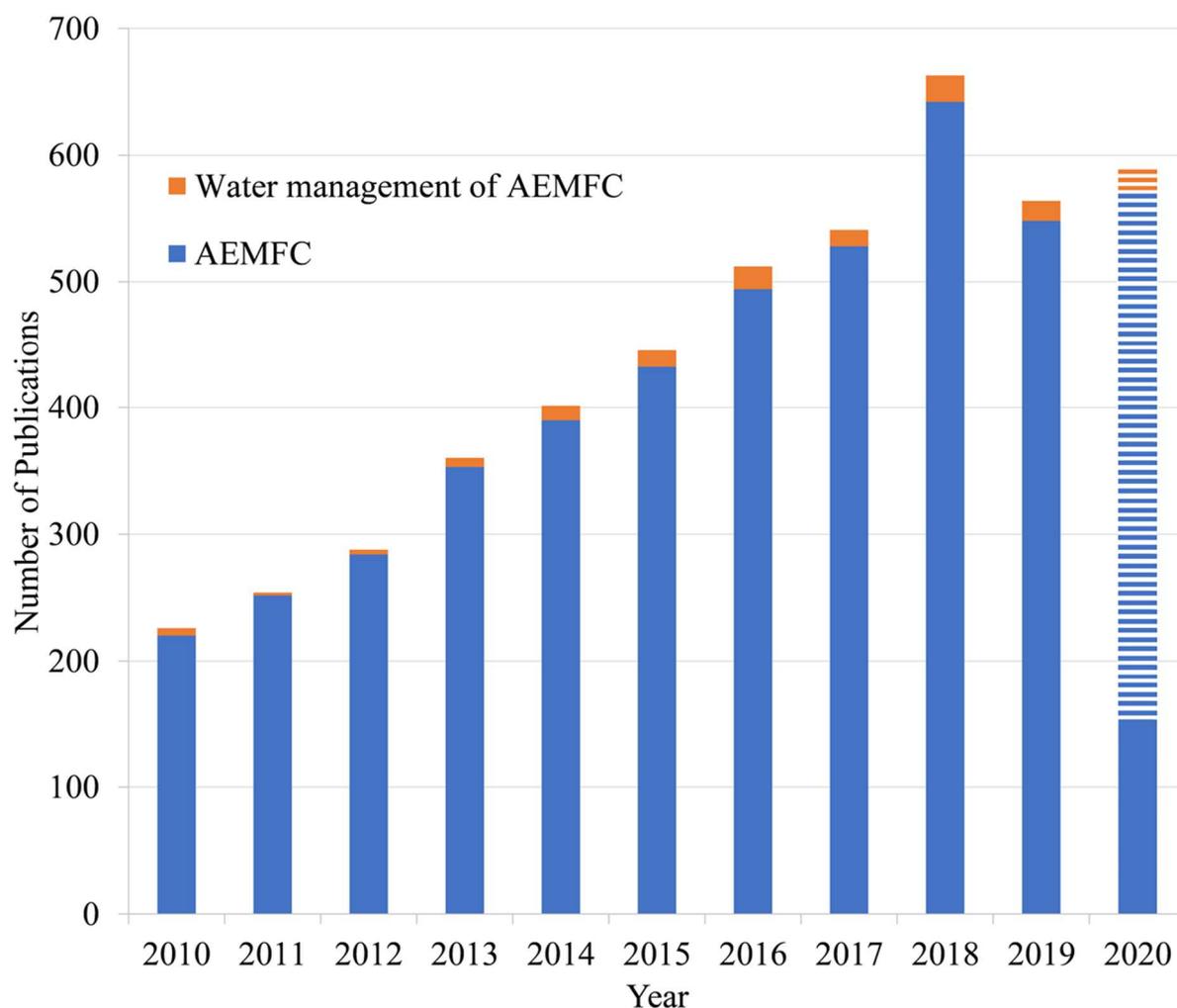
1. Introduction

Electrochemical energy conversion devices such as fuel cells are believed to be an ideal power source to meet the global energy demand which is increasing rapidly[1]. The high efficiency of fuel cells, fast recharging capacity compared to batteries and their benign environment impact are the major driving force for the development of fuel cells [2]. In addition, the operation of fuel cell only produce water as byproduct unlike traditional combustion engines which emits hazardous gases and fine particles[2–5]. Furthermore, fuel cells offer silent and vibration free operation as there are no moving parts unlike in combustion engines [7]. Fuel cells are classified into various types depending upon the type and nature of the used electrolyte and the operating temperature range. Among them, Alkaline fuel cells (AFCs) were the first to be developed in 1950s by NASA for space applications. An electrolyte solution of potash made it possible to reduce the corrosion issues encountered with the acid medium. But this technology has various disadvantages such as the formation of carbonate when CO₂ of air in contact with alkali electrolyte restricting the gas diffusion and water transport and a fluidic management of the circulating electrolyte which is quite complicated to implement [7-9]. This technology has been partially supplanted by PEMFCs when a dedicated sulfonated tetrafluoroethylene based fluoropolymer-copolymer called Nafion appeared in the late 1960s. GenCell Inc. still commercializes a liquid electrolyte technology thanks to a well-designed system, especially to eliminate CO₂ from the air, a robust technology showing no problem of humidification or frost and low cost. However, the low power density of these AFC systems and therefore the resulting ground footprint limits their range of applications.

More recently, AFCs which use an anion exchange membrane (AEM) are becoming a well-developed and very promising technology as there is no problem of electrolyte leakage [10]. Although AEMFC is the mimic of PEMFC technology, the principle difference between them is the nature of their mobile ions (OH^- in AEMFC, H^+ in PEMFC); the cell atmosphere being basic in AEMFC and acidic in PEMFC. Although PEMFC received greater attention from the researchers and good amount of funding from various government and private organizations for their development, the cost of the PEMFC system is major hindrance for its day to day applications. This cost mainly arises from the expensive Pt based electrodes and the electrolyte Nafion. In this context, AEMFC has been identified as a competitor that can use a platinum group metal (PGM) free catalyst such as nickel [11,12] and less expensive electrolytes. Further, oxygen reduction reaction (ORR) is more favorable in alkaline electrolytes reducing the ORR overpotential and allowing to use lower catalyst loading contributing to reduce environmental pollution [13,14]. The other benefit of AEMFC is that alkaline cell atmosphere give raise a possibility to adopt broad category of materials as bipolar plates and other cell components[8,10,14-16].

In spite of fascinating advantages of AEMFCs, some challenges must be overcome in terms of materials properties and operational parameters to catapult this system to the forefront of competitive technologies regarding energy conversion devices. Low anion conduction and poor durability of AEM[17], carbonation when exposed to CO_2 [18] and water management of the system[19] have been pointed out as the main factors impacting AEMFC performances. Water management is especially critical because of its intrinsic imbalance across various parts of the cell and a proper water management implies long-term and stable cell performance [20] . Moreover, low water content in the cell often leads to poor ionic conductivity and degradation of AEM while too much water leads to flooding of electrodes arising mass transport issues particularly at higher current densities. On the contrary, in PEMFC, water management is

largely explored from the two past decades [21–26]. However, water management in AEMFC has been overlooked from several years and most of the research is focused on developing high ionic conducting and durable AEMs [26-30] and non-Pt catalysts for hydrogen oxidation (HOR) and ORR[31,32]. These delivered efforts helped in enhancing performances of AEMFCs but these latter remain below those of PEMFCs. In recent times the research community has realized the importance of water management in AEMFC. The conducted simulation and



experimental studies during these last five years have revealed the real potential of this subject that has to be pursued in future years. Figure 1 represents the number of publications reported in the last decade (from 2010 to 2020) on AEMFCs and water management, the linear growth in number of publications further justifies the importance of AEMFC and water management.

Figure 1. Year wise number of publications appeared in AEMFC and water management in the last ten years from Web of Science using the key words “AEMFC” or “water management and “AEMFC”. The publication number in 2020 is a projected value based on the number of articles published until April 2020.

In this review, we make an effort to rationalize the important contributions to achieve high performing AEMFCs through effective water management. The results reported so far in the literature include challenges in AEMFCs [31,32], performance achieved so far [33,34], developments of AEMs [35–37] and aspects related to the used electrocatalyst [38,39]. Very recently, C.E. Diesendruck *et al.* described the role of water towards AEMFC stability in their review [40]. However, water management was not explored adequately yet. Our group has been working on water management issues in PEMFC and a significant contribution was made in terms of numerical and experimental studies [41–46]. With the knowledge gained from water management strategies, we formulate this review and we believe that it will enhance the knowledge and understanding of water management mechanisms in AEMFCs and a motivation for the upcoming studies on this subject.

2. General principle of AEMFC

The general structure of an AEMFC is very similar to that of a PEMFC comprising an anode and a cathode. An AEM is sandwiched between two electrodes to form a membrane electrode assembly (MEA) and it is supported by gas diffusion layers (GDLs) on either side [47]. The fuel hydrogen is fed at the anode and gets oxidized while the cathode is fed with oxygen and it gets reduced in presence of water to produce hydroxide ions. The AEM transports these ions to the anode where they combine with hydrogen ions to produce water as shown in Eq.1, Eq.2 and Eq.3 for the reaction occurring at the anode, at the cathode and the resulted net reaction, respectively [48].



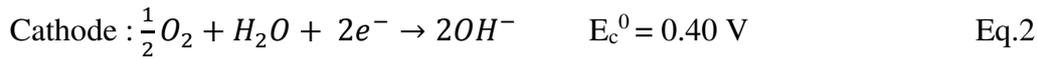


Figure 2 illustrates the schematic representation of AEMFC and PEMFC highlighting the differences between them. One can especially notice that mobility of ions is from cathode to anode and water is needed for ORR at the cathode in the case of AEMFC.

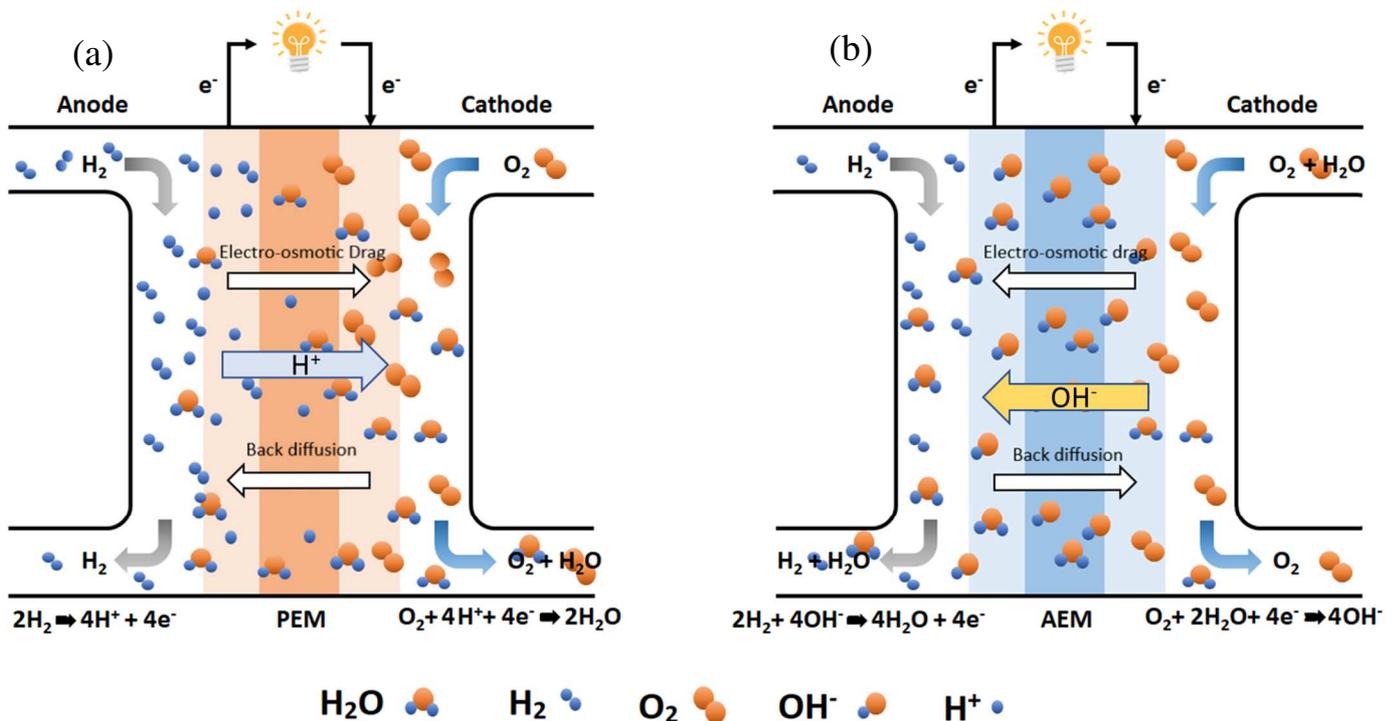


Figure 2. Schematic representation of (a) PEMFC and (b) AEMFC highlighting the differences between them.

In contrast to PEMFCs wherein water is only generated at cathode during ORR, in AEMFC water is generated and consumed electrochemically during HOR at the anode and ORR at the cathode, respectively. This gives rise to a significantly different scenario occurring quantitatively in AEMFC and PEMFC. For every $4 e^-$ transferred, there are 4 water molecules generated (anode) and 2 water molecules are consumed (cathode) in AEMFC, while in PEMFC for every $4 e^-$ transferred only 2 water molecules are generated at the cathode. This distinct

behavior in water production and consumption between the two systems implies that water management strategies employed in PEMFC may not be suitable for AEMFC. In fact, water management is more important in AEMFC as it represents a greater imbalance across the cell.

3. Water management strategies

3.1. Materials for water management

For the effective water management, the properties of various components of AEMFC have to be optimized. The emphasis should be given to water uptake of membranes, ionomers in catalyst layers (CLs), polytetrafluoroethylene (PTFE) content in GDL, electrode formulation (choice of catalyst and ionomer, ratio of catalyst/ionomer/carbon for instance). Each of these materials/parameters are described in the following sections highlighting the efforts made in terms of water management.

3.1.1 Gas diffusion layers

Similarly to PEMFCs, GDLs are critical component of in AEMFC system since they have multiple functions and they are the supporting material for MEA [49]. GDLs are designed to have properties *viz* high gas permeability to transport the reactant gases to the CL and they should be optimized to balance hydrophobicity -to expel water out of the cell- and hydrophilicity -to retain water and keep the membrane sufficiently hydrated- [50], They should also high electronic conductivity to drive the electrons from CL to the circuit; in addition, high thermal and chemical stability under vigorous conditions [53-55]. Woven carbon fibers or cloths are generally accepted as GDL substrates through which gases are transported to CL, and these are treated with PTFE to be hydrophobized and prevent the accumulation of liquid water [52,53]. As GDL is in direct contact with CLs where the water is produced and consumed, its proper engineering is important to manage water. Several strategies, discussed in more details in the following section, have been proposed to fabricate an ideal GDL to manage the liquid water effectively in the cell, including altering microstructure, varying hydrophobicity,

inclusion/exclusion of hydrophobic microporous layers, adding hydrophobic and/or hydrophilic additives [54].

Since wetproofing of GDL affects the water distribution in the MEA, variation of wetproofing of GDLs was explored by varying PTFE loading. From the knowledge of PEMFC water management strategies, it is believed that the addition of a small amount of PTFE in the anode GDL mitigates the flooding of anode by rejecting the excess water that occupies the pores of GDL causing fuel starvation [58-60]. Addition of PTFE affects the intrinsic properties of GDL such as porosity, and surface wetting properties which have significant impact on water distribution and reactant diffusivity. V.M. Truong *et al.* experimental results proved that an addition of 30% of PTFE in GDL (carbo papers CeTech Co., Ltd, Taiwan) is necessary to remove the liquid water effectively and to achieve optimized performance [57]. At such high PTFE, GDL becomes super hydrophobic (contact angle 142°) and expels the liquid water by shear force causing lower liquid saturation with improved gas transport. T.J. Omasta *et al.* proved a significant improvement in AEMFC performance when shifted from no PTFE Toray TGP-H-060 GDL to a 5 % PTFE loaded GDL at both anode and cathode [58]. In contrast, R.B. Kaspar *et al.* observed high performance by using GDLs (Torey carbon papers) without PTFE compared to PTFE loaded GDLs in their experimental study of AEMFC operating with 100 % RH at 60°C [59]. According to the authors, when anode GDL was coated with PTFE, the porous network of GDL was disturbed leading to increase flooding which had severe effects on cell performance while the addition of PTFE in cathode GDL showed minimal effects. The authors pointed out that an addition of 10 % of PTFE in anode GDLs completely blocked the porous network and alleviated the flooding at moderate RH causing performance degradation. This conclusion is totally opposed to the results by V.M. Truong *et al.* who claimed that a PTFE treatment could create a new hydrophobic porous network in GDL which did not held liquid water (dry pores). Hence, the exact effect of PTFE on GDL porous structure is still debatable,

however at low RH, or with thicker AEM, addition of a small amount of PTFE in GDL could be beneficial.

The inclusion of a micro porous layer (MPL) between GDL and CL was another strategy used to manage liquid water and that approach was widely considered in PEMFC to overcome the flooding of cathode [60,61]. The typical MPLs employed in fuel cells were carbon layers (carbon black, CNTs etc) bonded with PTFE [60,61]. They do not only serve the purpose of water management but also provide a good electrical connectivity between CL and GDL and induce a uniform distribution of reactant gases to CL [64]. The MPL is not just a barrier to liquid water, it also plays the role of thermal resistance to maintain a temperature gradient between the electrode and the GDL/plate so as to allow diffusion of water vapor along with saturation pressure gradient [44,46]. Since AEMFC is analogous to PEMFC the same strategy was also practiced by many researchers to eliminate anode flooding in AEMFCs [65,66]. For example H. Deng *et al.* developed a whole-cell 3D multiphase non-isothermal model to study the effect of MPL assuming the liquid water in both anode and cathode flow channels was zero [66]. It was evidenced that the inclusion of MPL at the anode side had a positive effect while at the cathode side a negative effect was shown on cell performance. The MPL at anode helps in managing excess water by back diffusion to cathode, while it makes the situation much worse at cathode causing further dehydration at AEM-cathode interface and ionomer in cathode catalyst layer (CCL) leading to increasing the Ohmic resistance. Figure 3 shows voltage and power density data under different MPL configurations namely MPL at both anode and cathode (ACMPL), MPL only at anode (AMPL), MPL only at cathode (CMPL) and no MPL. From the results presented in the figure, one can notice that inclusion of AMPL delivered highest power while inclusion of CMPL delivered lowest power supporting the fact that removal of water at anode and maintaining adequate hydration at cathode were crucial to achieve high performance in AEMFC[67].

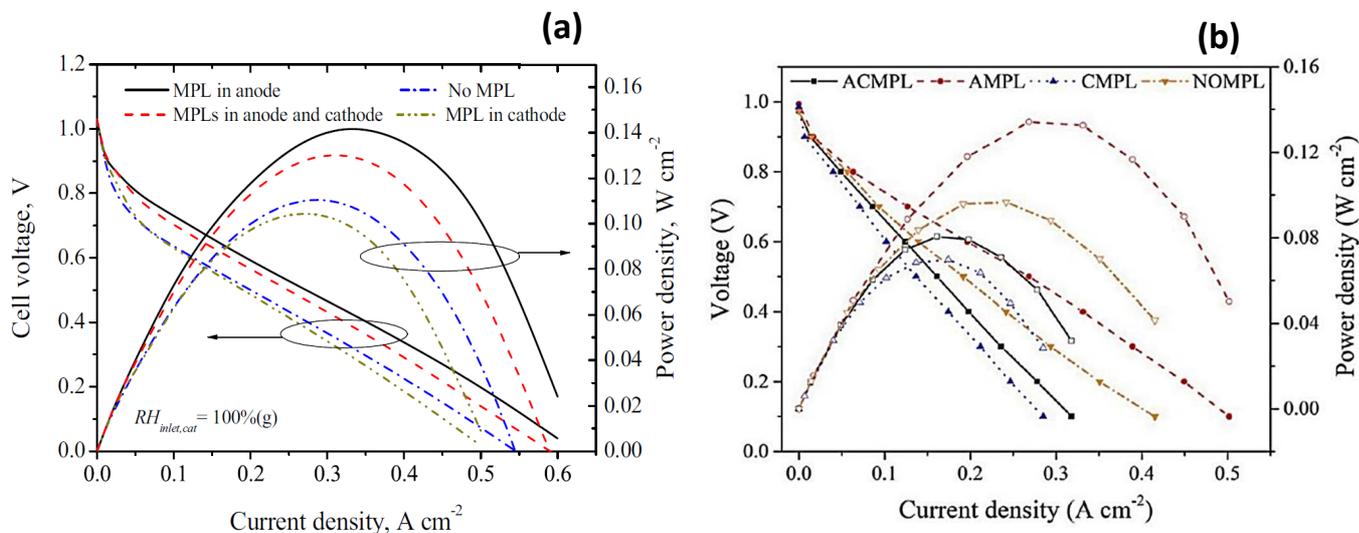


Figure 3. Voltage and power density of AEMFC obtained at different MPL configurations at 100% RH and ambient pressure in (a) simulation study and (b) experimental study. Reproduced with permission from Ref. [65] and [67]

On the other hand R.B. Kaspar *et al.* modeling studies presented a totally different scenario wherein inclusion of MPL at anode side or at both sides had negative effects on cell performance [59]. They estimated that even small amount of PTFE in MPL made it denser blocking the pores and resulting in ineffective removal of water from electrode surface. Their explanation based on the pore size evolution was also convincing and further optimizations in terms of PTFE content in MPL are necessary to conclude regarding the effect of MPL on cell performances.

3.1.2 Electrode fabrication and architecture

Electrodes are an important constituent of AEMFC since they are responsible for HOR at the anode and ORR at the cathode. To be specific these reactions occur at the triple-phase boundary where the reactant is in contact with catalyst and AEM [13,34]. It has been widely reported that non-Pt catalysts such as transition metals oxides (MnO, Co₃O₄ etc) [71-75]

chalcogenides (CoS, MoS₂ etc.) [16,70,71] and carbon nanomaterials (graphene, MWCNTs and their derivatives) [40,78-81] could be employed as electrocatalysts in AEMFC. Since none of them is really commercialized, the state of art is based on Pt supported on carbon black with an anion exchange ionomer (AEI). CLs play a vital role in water management as water is produced and consumed in its thickness. Hence intrinsic properties of catalysts, the type of catalyst support and AEI as well as the topology have to be optimized to achieve high performance in AEMFCs.

H.S. Shiao *et al.* showed breakdown of various polarization losses at 100 % RH (Figure 4) using a multi-phase model and they revealed that although ORR loss was dominant, one should not neglect the HOR loss as it is significant unlike in the PEMFCs where HOR loss is considered as negligible [73]. Coming to Ohmic loss, although AEM contributes mostly to ionic resistance, the CCL also shows significant Ohmic loss due to local dehydration caused by water consumption in ORR. Optimization of catalyst loading is an important step to achieve water management across the electrodes as it impacts on the porosity and thickness of CLs and thereby distribution of water and reactant gases. A systematic study on the effect of Pt loading on the cell performance was presented by D. Yang *et al.* [74]. The authors tested CLs with different Pt loadings and they found that the optimum loading was 1 mg/cm² (using 70% Pt/C) at which the electron transfer and mass transfer had lowest activation energy. By increasing the Pt loading beyond this, the cell showed drop in performance because of an increase in the thickness of CL. Conversely, it was believed that increased Pt loading could enhance the number of catalytic sites and thereby the performance [75]. Nevertheless, the scenario was different when coming to practice since poor dispersion and low utilization of catalyst particles beyond an optimum loading were observed. Further increasing in electrode thickness could contribute to larger activation and Ohmic losses as the electrons, ions have to travel over a longer distance [76].

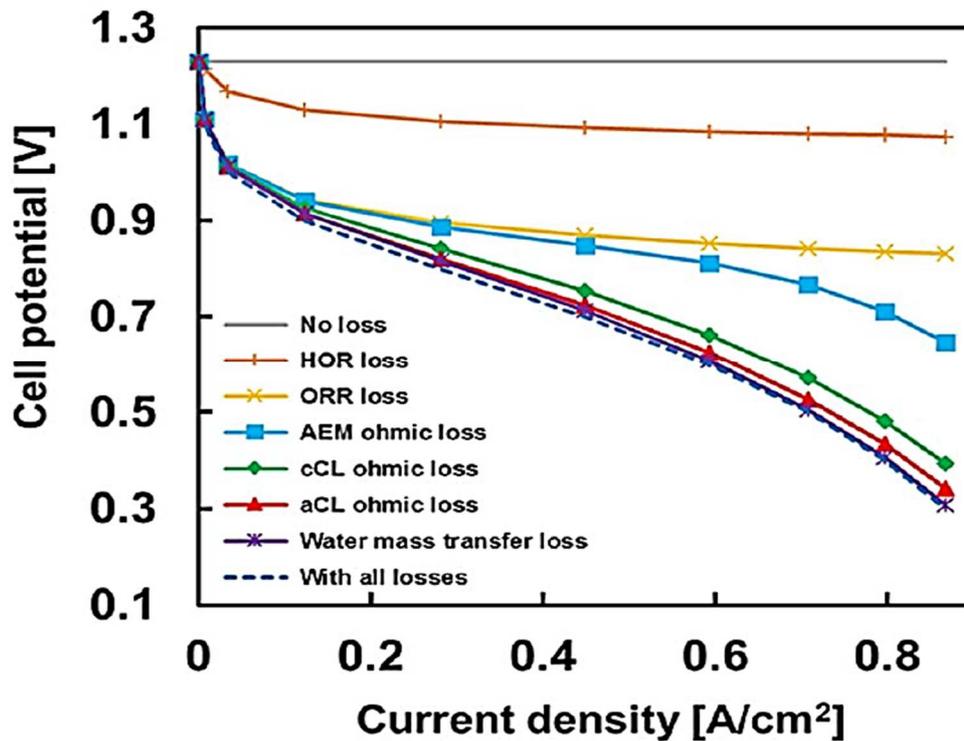


Figure 4. Various polarization losses in AEMFC operating at 60 °C with 100 % RH. Reproduced with permission from Ref. [73].

Further at high RH, hydrogen mass transport losses were significant as the excess water at ACL occupied the pores and reducing hydrogen transport. Such losses were mitigated by using high porosity ACL. For instance, liquid fraction in ACL was reduced from 1 to 0.9 when the porosity is changed from 0.35 to 0.6 and thus average hydrogen mole fraction was almost doubled in ACL [55]. Replacement of Pt with Pt-Ru at the anode was generally proposed to achieve high performance in AEMFCs as Pt-Ru offered moderate interaction with hydrogen resulting in optimized binding energy on the its surface compared to Pt wherein hydrogen

adsorption is relatively stronger [77]. Generally, Ru was added by keeping same Pt and AEI loading on the electrode. However, this strategy relatively reduced the amount of carbon in the electrode resulting in thinner and less porous CL promoting the flooding [20]. The porosity can be improved by increasing the carbon loading as observed by T.J. Omasta *et al.*. They increased carbon loading (from 0.45 to 0.71 mg/cm²) and reduced ionomer content from 20 wt.% to 17.2 wt.%. This strategy improved the peak power density to 1.7 W/cm² from 1.4 W/cm² (standard method) wherein the increased pore volume and the water retention capacity played a key role [20]. Further improvement in cell performance was observed by increasing both AEI and carbon content by maintaining the same AEI:carbon ratio which lead to a thicker CL with an improved pore volume. That means the water capacity of the anode was increased and was clearly reflected in cell performance wherein the highest record performance of 1.9 W/cm² was observed. Based on these strategies the ratio of AEI:C:Pt was optimized as 0.94:2.5:1 to design a high performing AEMFC anode with a catalyst (Pt-Ru) loading of 0.71 mg/cm².

M. Mamlouk *et al.* studied the effect of cathode thickness by varying the Pt/C ratio (30,40 and 60 %) at a loading of 0.4 mg/cm² [78]. On one hand, altering Pt/C resulted in different thicknesses of the CL, *i.e.* at 60 % the CL formed a thin layer compared to that prepared at lower ratios. On the other hand, the surface area was found to be higher for the smallest ratio resulting in smaller average particle size. When AEMFC was operated with Pt/C of 30 %, the kinetic reaction region shifted to higher potentials compared to Pt/C of 40 and 60 %. This increase in electrode kinetics is due to lower average particle size and enhanced electrochemical surface area. Nevertheless optimum thickness of cathode was found to depend on oxygen partial pressure and the ionomer properties [79]. Further, two different anodes were tested with Pt/C of 60 and 20 % with an effective Pt loading of 0.4 mg/cm². As mentioned above higher ratio yielded thin catalyst layer resulting in lower IR losses at intermediate

potentials but a significant loss was observed at lower potentials due to ineffective water management and similar effect was also observed regarding flooding of PEMFC cathode [80].

Understanding and quantifying hydrophilic properties of CL is indeed important to estimate water holding or rejecting capacities of CL. S. Huo *et al.* studied the effect of CCL wettability on the performances of AEMFC [65]. The cell performances were simulated by varying the contact angle (from 80 to 110°) of the CCL. The performances were high at lower contact angle 80° (hydrophilic) wherein CCL attracted and retained more water from the ACL by back diffusion. This effect lead to decrease the activation and Ohmic resistance of the cell by providing adequate water for ORR and to hydrate the AEM. Further experimental studies by D. Yang *et al.* found there was tradeoff between hydrophobicity and electronic conductivity in CL [74]. A series of experiments were conducted by varying PTFE content (hydrophobicity) from 10 to 40 % in both CLs. Although the increase of PTFE content in CL enhanced the water management but beyond an optimum level it diminished the electronic conductivity of CL as PTFE is a pure insulator. This was further supported by cell performance data wherein increasing PTFE loading from 10 to 20 % had a positive effect while further increasing it to 30 and 40 % had a negative effect.

Apart from the porosity and hydrophobicity of CL, characteristics of ionomer in the CL has been shown to have a substantial influence on electrode water management. Similar to proton exchange ionomer (generally Nafion) in PEMFCs, an AEI is needed to facilitate ionic transport between various reaction sites in CL and membrane [81]. Thanks to fuel cell market, there are few companies producing commercial AEIs, among them Tokuyama AS-4, FAA-3 (Fuma-Tech) ionomers were well explored in the literature as reference ionomers to fabricate AEMFC electrodes. Many other ionomers based on functionalized polysulfone, radiation grafted polymers were studied in the lab scale point of view [82–84]. An optimum level of ionomer in the electrodes is indeed important to achieve high performance in AEMFCs. A too

low ionomer content often lead to discontinued channels for hydroxide ion conduction in CL which increases IR loss and ineffective utilization of catalyst due to lower accessible electrochemical surface area while too much ionomer accelerates electrode flooding as the ionomer is mostly hydrophilic in nature and reduces the pore volume available for oxygen gas diffusion, suppressing the electronic conductivity of CL [85]. D. Yang *et al.* suggested an optimum loading of ionomer is about 20 % at which the maximum power output was observed compared to 15 and 25 % ionomer loading [86]. This finding was also supported by R.B. Kaspar *et al.*, their work on ionomer optimization [59] proved that electrode microstructure properties were greatly altered by the ionomer content and hence it is important to consider ionomer to catalyst ratio while designing the electrodes.

3.1.3 AEM

As mentioned above, AFC research has been accelerated after replacing the liquid electrolyte with a solid polymer electrolyte called AEM [8]. In a typical AEMFC design, AEM is sandwiched between the anode and the cathode and plays multiple roles such as a gas separator, ion conductor from cathode to anode, electronic insulator [87]. To develop high performance AEMFC, it is desired to have a membrane with good hydroxide conductivity mechanical and thermal stability under operating conditions and membranes should be stable enough in strong alkali conditions [88]. In spite of significant achievements on conductivity and stability [87,89–91], the research is still in progress to optimize properties of AEM. Table 1 shows the recently developed AEMs and their performance under several experimental conditions such as temperature, RH, and flow rate.

Table 1 AEMs reported in the literature and peak power density of AEMFCs depending on different operating parameters.

Author, Year	AEM	Catalyst loading (mg/cm ²)	Temperature (°C)	RH, flowrate, Back pressure	Power density (mW/cm ²)	Ref.
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Liu <i>et al.</i> (2019)	PAEK*-MmOH	0.4	60	100 % 200 200 mL min ⁻¹ 0.1 MPa	302	[92]
Zhang <i>et al.</i> (2019)	PBFB*	0.5	60	100% 1000 1000 mL min ⁻¹ NB	133	[93]
Wang <i>et al.</i> (2019)	PAP*	1	95	100% 151 951 mL min ⁻¹ 250 300 kPa	920	[94]
Huang <i>et al.</i> (2019)	PNB* copolymer	NR	80	NR	3,400	[95]
Chen <i>et al.</i> (2018)	(TC-QAPPO)* / (QA-LDH)*	0.5	60	100% 100 200 mL min ⁻¹ 100 kPa	267	[96]
Omasta <i>et al.</i> (2018)	(ETFE- BTMA)*	NR	60	100% 100 100 mL min ⁻¹ NB	1,900	[20]
Omasta <i>et al.</i> (2018)	ETFE-g-poly (VBTMA*)	0.6	60	87 79% 100 100 mL min ⁻¹ NB	1,400	[58]
Pivovar <i>et al.</i> (2018)	Gen 2 novel perfluoro(PF) AEM	0.5	60	80% 1000 1000 mL min ⁻¹ NB	1,400	[71]
Wright <i>et al.</i> (2016)	(HMT-PMBI*)	0.4	60	100% 200 200 mL min ⁻¹ NB	370	[97]
Zhu <i>et al.</i> (2016)	(PPO*)-based AEM (T20NC6NC5)	0.4	60	100% 250 250 mL min ⁻¹ 0.1 MPa	36	[98]
Lai <i>et al.</i> (2016)	(C – HPPEs – 4/1*)	1	80	100% 100 50 mL min ⁻¹ NB	83.6	[99]
Chen <i>et al.</i> (2016)	(aQAPSF*)	0.4	60	100% 250 250 mL min ⁻¹ 0.1 MPa	610	[100]
Espiritu <i>et al.</i> (2016)	BPI* 74.6% DOG	NR #	50	100% Stoichiometry 1.2 2.2 NB	608	[101]
Yan <i>et al.</i> (2016)	PEEK-ImOH	0.5	60	100% 20 10 mL min ⁻¹ NB	120	[102]
Pivovar <i>et al.</i> (2016)	Gen 1 novel perfluoro(PF) AEM	0.4	60	100% 200 200 mL min ⁻¹ NB	430	[76]
Deng <i>et al.</i> (2016)	Tokuyama A201	0.5	50	100% 500 1000 mL min ⁻¹ NB	NR	[77]
Jia <i>et al.</i> (2016)	Co-OH-CO ₃ nanoneedle arrays	0.1 0.02	50	100% 100 200 mL min ⁻¹ 0.2 MPa	113	[103]
Omasta <i>et al.</i> (2016)	ETFE-g-poly (VBTMAC*)	0.6	60 – 70	90 – 100% 1000 1000 mL min ⁻¹ NB	1,400	[104]

Kaspar <i>et al.</i> (2015)	Tokuyama A901	0.4	80 60	100% 200 200 mL min ⁻¹ 250 kPa	737 459	[105]
Yang (2014)	(NBA*) – Tokuyama A201	0.4	50	100% 100 200 mL min ⁻¹ 0.05 kPa	407	[106]
Yang (2014)	Tokuyama A201	0.2 1	50	100% 100 200 mL min ⁻¹ 0.05 kPa	213	[74]
Khadke <i>et al.</i> (2014)	Tokuyama A201	0.07 0.16	60	100% stoichiometry 18 36 NB	90	[107]
Wang <i>et al.</i> (2014)	(aQAPSF)*	PtRu/C 0.26 PtRu/C 0.13	60	100% 400 400 mL min ⁻¹ NB	1,000 870	[77]
Zhao <i>et al.</i> (2013)	PTFE membrane based with Polyvinyl benzyl hydroxide (TPPVBN)	0.4	60	100% 100 200 mL min ⁻¹ 0.05 kPa	348	[108]
Mamlouk <i>et al.</i> (2012)	Aminated poly (LDPE) g – VBC*	0.4	60 50 20	100 % NR	823 718 648	[109]
Isomura <i>et al.</i> (2012)	Tokuyama	NR	80	100% RH 200 200 mL min ⁻¹ NB	730	[92]
Zeng <i>et al.</i> (2011)	(t-PVBTMACl)*	0.5	50	100% 400 400 mL min ⁻¹ NB	210	[19]
Wang <i>et al.</i> (2011)	PTFE based polysulfone (PTFE-QDPSU)*	0.5	50	100% 80 100 mL min ⁻¹ NB	146	[110]
Luo <i>et al.</i> (2011)	(QPMBV-APE)*	0.4	70	80% NR	180	[111]
Cao <i>et al.</i> (2011)	(qPBV)*	0.8	15	100% 80 100 mL min ⁻¹ NB	156	[112]
Pianaa <i>et al.</i> (2010)	Acta I2	0.5	50	85% 1000 2000 mL min ⁻¹ NB	400	[113]
Pan <i>et al.</i> (2010)	(QAPS)*	4	6	100% 50 50 mL min ⁻¹ NB	100	[82]
Gu <i>et al.</i> (2009)	(TPQPOH)*	0.5	80	100% 200 200 mL min ⁻¹ 250 kPa	141	[114]
Reshetenko <i>et al.</i> (2017)	Tokuyama A201	0.2	60	100% 200 200 mL min ⁻¹ NB	280	[115]
Isomura <i>et al.</i> (2011)	Tokuyama	NR #	50	NR 200 200 mL min ⁻¹	330	[116]

				NB		
Zhao <i>et al.</i> (2013)	QAPS/PTFE	0.4	50	100% 100 200 mL min ⁻¹ NB	315	[117]
Vijayakumar <i>et al.</i> (2015)	QPSU/QSBA-3	anode 0.25 cathode 0.4	60	80% 300 500 mL min ⁻¹ NB	300	[118]
Vinodh <i>et al.</i> (2015)	QPSU/10% SiO ₂	anode Pt- Ag/C 0.5 cathode 0.375	60	NR 20 40 mL min ⁻¹ NB	150	[119]
Zeng <i>et al.</i> (2013)	DAPSF	0.6	60	NR	342	[120]
Arges <i>et al.</i> (2012)	PSF-TMA-OH ₋	0.5	60	95% 200/ mL/min NB	180	[121]
Cheng <i>et al.</i> (2016)	PSf-GIm- MImOH ⁻ 140%	0.5	50	100% NR NB	39	[122]
Iravaninia <i>et al.</i> (2017)	PSF THMDA	0.5	60	100% 100 200 mL min ⁻¹ NB	11	[88]
Zhao <i>et al.</i> (2014)	ACDH96	0.4	50	100% 100 200 mL min ⁻¹ NB	370	[123]

NR: Not reported, NB: No back pressure applied

* PAEK: Poly (aryl ether ketone), PAP: poly(aryl piperidinium, PNB: poly(norbornene), TC-QAPPO: triple-cation side chain poly(2,6-dimethyl-1,4-phenylene oxide), QA-LDH: quaternary-ammonium-modified layered double hydroxide, QAPPT: quaternary ammonia poly (N-methyl-piperidine-co-p-terphenyl), BTMA: Benzyl trimethyl ammonium, VBTMA: (vinylbenzyltrimethylammonium), PPO (poly(2,6-dimethyl-1,4-phenylene oxide), aQAPSF: Self-aggregated quaternary ammonium polysulfone, C – HPPEs – 4/1: Crosslinked heptamethyl phenolphthalein-containing poly(arylene ether sulfone), NBA: n-butyl acetate, TPQPOH: polysulfone-methylene quaternary phosphonium hydroxide, QPMBV-APE: Quaternized poly (methyl methacrylate-co-butyl acrylate-co-vinylbenzyl hydroxide), PBV: Poly (vinylbenzyl hydroxide). PSf-GIm-MImOH: Poly sulfone-guanidinoimidazole-methylimidazole OH form, QPSU: Quaternized polysulfone, PSF-TMA-OH : Polysulfone trimethyl ammonium OH form, TMHDA: N,N,N¹,N¹-tetramethyl-1,6-hexanediamine, DAPSF: diamine cross-linked quaternized polysulfone.

The general structure of an AEM comprises a polymer backbone and ion exchange sites (IES) as functional groups or side chains which act as conduction path for hydroxide transport. In general, quaternary ammonium cations are commonly used ion exchange sites due to their simple preparation methods and high ion exchange capacity [133-136]. It is desired to have AEMs with high IES in order to have high ionic conductivity. However, AEM with high IES often leads to swelling which deteriorates its mechanical properties, and it is obvious that the degradation of anion exchange groups and polymer backbone is more likely to happen in alkali environment, hence a robust morphology is critical and is trade-off between ionic conductivity,

dimensional and chemical stability [7,124,125]. In addition, OH^- conductivity of AEM is highly dependent on water, for instance, the state of art on FAA-3 membrane shows more than ten times increment in through-plane ionic conductivity when measured at 90% RH compared to 50% RH as shown in Figure 5 [128].

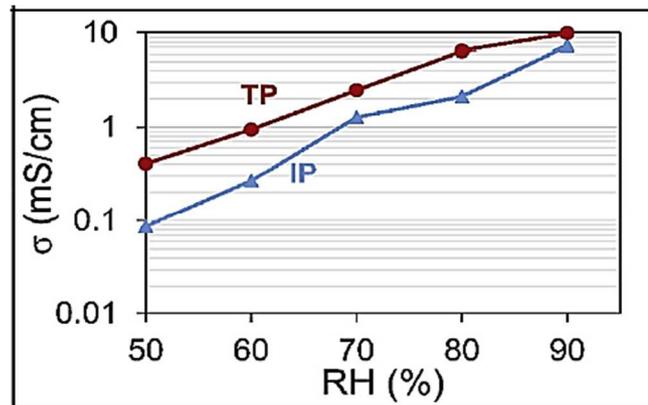
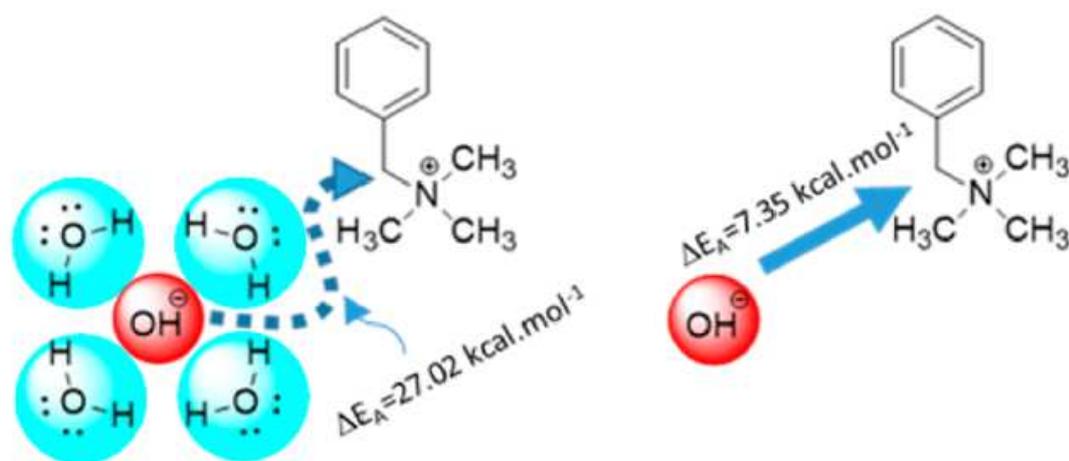


Figure 5. In-plane (IP) and through-plane (TP) hydroxide conductivity of FAA-3 membrane as function of RH. Reproduced with permission from Ref. [128].

As the quaternary ammonium cations might be attacked by OH^- in dry state (see later), the hydroxide conductivity cannot be measured through the entire range of RH as for protonic conductivity in the case for PEMFC. Based on this fact, one supposes that water plays a crucial role in the transport of hydroxide ions within hydrated AEMs. The exact mechanism of hydroxide conduction in AEM is still debatable. The Grotthuss mechanism (which is defined as the movement of hydroxide ions through hydrogen bond network of water molecules) is favored in such hydrated AEMs over the vehicular mechanism [129–131].

Further, the chemical stability of AEM is also influenced by the hydration level and most of the experimental work already prove that the degradation of AEM is sever under dehydrated conditions. R. Dekel *et al.* [132] studied the degradation of quaternary ammonium cations (QA) namely trimethylbenzyl ammonium bromide (TMBA), triethylbenzyl ammonium

chloride (TEBA) with respect to hydration number (λ) (defined as a number of water molecules per OH^-). These QAs are the main constituents of AEMs and AEIs, hence understanding their behavior in aqueous media in turn helps to assess the behavior of AEMs and AEIs. The literature reports prove that TMBA is more stable than TEBA due to their different degradation mechanisms [133,134]. The former degrades through a SN^2 mechanism where hydroxide ions react with carbon atoms attached to nitrogen. The later degrades through Hoffmann elimination wherein hydroxide ions attack the hydrogen ions in beta position of nitrogen. Ex-situ stability tests were conducted with different hydration levels to assign their stability. Degradation was reported to be quite rapid for both QAs when there was no water ($\lambda=0$), while TMBA showed fair stability when λ value was increased to 4 and full stability (no degradation) at λ value equal to 8. On the other hand TEBA achieved fair stability at λ value to 8 (200 times more stable than for $\lambda = 2$) [135]. It is noteworthy that at a certain point of hydration level even unstable QA could be quite stable proving that the solvation of hydroxide has significant effect on degradation of QAs. Figure 6 represents the effect of solvation on the nucleophilic attack of



OH^- clearly. This work revealed that OH^- attack was quite rapid in the absence of water, while in presence of water OH^- were shielded by water molecules (steric hindrance) and was less prone to attack the QAs [132].

Figure 6. Schematic diagram of nucleophilic attack onto TMBA with and without water. Reproduced with permission from Ref.[132].

However, further studies are required to accept these conclusions as they are drawn based on ex-situ stability test results of QAs, but the AEMs and AEIs eventually contain polymeric backbones along with the QAs. Further, AEMs and AEIs experience significantly different atmospheres when operated in AEMFC with respect to mechanical stress, temperature, hydration which are not considered in the above studies.

Apart from conductivity and durability, one key parameter namely water transport through the membrane that dictates the cell performance has to be considered. As AEM is in between the water production zone (anode) and water consumption zone (cathode), it experiences a severe water imbalance. It is to be noted that water moves through the AEM in both directions i.e. from cathode to anode by electro-osmotic drag and from anode to cathode by back diffusion. In fact, it is well established that the majority of the water consumed in ORR at cathode is transported through AEM from the anode, hence an AEM with high diffusion is favorable to establish water equilibrium between anode and cathode. However high water uptake often leads to swelling and mechanically inferior AEMs. M. Mandal *et al.* used light crosslink of AEMs to control the swelling and developed a robust AEMs based on poly (norbornenes)[136]. This AEM offered excellent mechanical stability with superior hydroxide conductivity (212 mS/cm at 80°C) and low water diffusion resistance. With these synergetic effects, the AEM delivered record high AEMFC performance of 3.5 W/cm² at 80 °C. Diffusion resistance of AEMs can also be tuned by controlling the hydrophilicity of the AEMs. X. Gao, *et al.* characterized water transport properties of poly (styrene–ethylene–butylene–styrene) based AEM as function of temperature and RH [137]. It was found that the water permeation flux through the AEM increased with temperature following the Fick's law of diffusion and was proportional to the water content gradient and diffusion coefficient. Besides, water

permeation flux was decreased with RH due to the decrease in water content gradient. However, the ex-situ test atmosphere is different than actual AEMFC as water is consumed at cathode resulting in increased water content gradient between anode and cathode thus improving the water permeation flux leading to proper water management of AEMFC. H. Zhang *et al.* used pore filled (PF) membranes as strategic candidates to have dominant water diffusion than electroosmosis drag [138]. They prepared a series of PF membranes by varying the weight ratios of 3-methacryloylamino propyl trimethylammonium chloride (MAPTAC) and styrene monomer as porous substrate and pore filler, respectively. PF1 (lowest *i.e.* 4.83 wt. % of MAPTAC) was highly hydrophobic membrane while PF4 (highest *i.e.* 100 wt.% of MAPTAC) was highly hydrophilic. For PF4, the amount of water moved from anode to cathode was larger than the others and this finding was further supported by the measured cell performance which showed flooding occurring in PF1 much earlier (15 mA/cm²) than in PF4 (90 mA/cm²).

The net water flux was reported to also depend on the thickness of the AEM [139] as the water diffusion mass transfer resistance is roughly equal to the ratio of the thickness to the diffusion coefficient. Optimizing it was another used strategy to deal with water management issues in AEMFC. It has been widely reported that thinner AEMs offers low Ohmic resistance [140–142]. Y. Oshiba *et al.* explored the relationship between thickness of vinyl benzyl trimethyl ammonium chloride (VBTAC) based AEMs and the cell performance [143]. They found that the thickness of AEM had the least influence on the performances at low current densities. In contrast, at high current density, thinner membrane (6 microns) performed much better than the thicker one (25 microns). P. Veh *et al.* followed a new strategy of direct membrane deposition (DMD) of catalyst layer on hexamethyl-p-terphenyl poly(benzimidazolium) AEM. Their direct deposition allows to fabricate the DMD as thin as 3 microns which greatly reduced the ionic resistance and improved the power density up to 1 W/cm² at 70 °C, while the traditionally used of GDE and free standing AEM method delivered

0.4 W/cm² as represented in Figure 7 [144]. The better performance of thinner AEM was not only attributed to low Ohmic resistance but also to a better water distribution across the cell as thin AEM is able to permeate the large amount of water generated at anode to mitigate anode flooding and cathode dry out at high current densities [142,145]. Thus thickness of AEM has critical influence on water dynamics of the cell and this is further supported M. Mandal *et al.* study [136]. They showed that the performances of AEMFC was drastically deteriorated upon increasing the thickness of the AEM from 10 to 30 μm . This negative effect was not just due to ionic resistance as ASR values are almost similar but due to low water transport from anode to cathode.

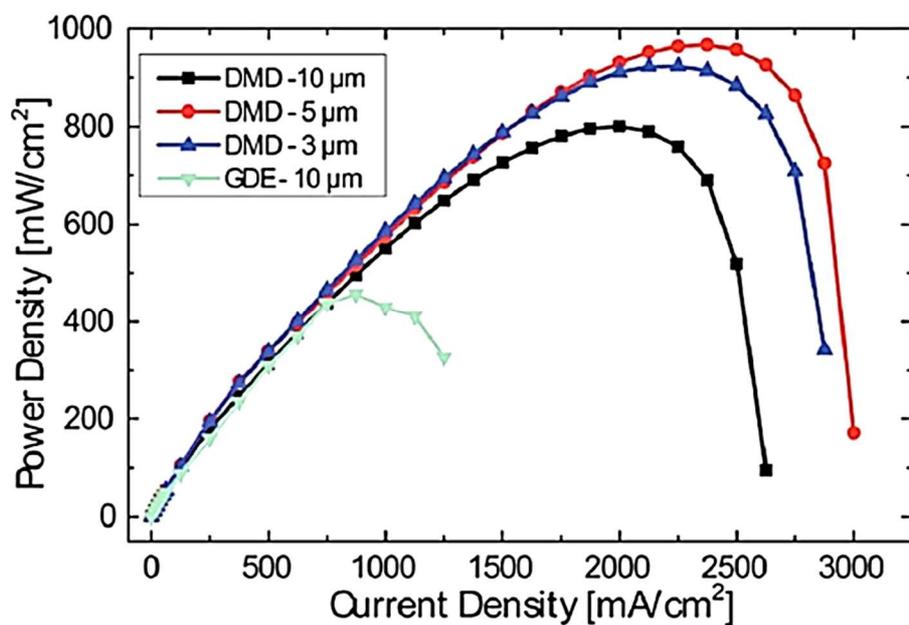


Figure 7. Power density of DMD cells with different membrane thicknesses (3, 5, 10 mm) and GDE with a 10 mm freestanding membrane. Reproduced with permission from Ref. [142].

Essentially, high water flux from anode to cathode is the most promising method to suppress anode flooding and mitigate cathode dry out. However, it is important to achieve a good balance between hydroxide/water transport and gas permeability, mechanical stability of the membrane [78]. From B. Eriksson *et al.* [146] studies, it was reported that the net transport of water through the membrane was from anode to cathode which invalidated the possibility of cathode dry out. However, there is always risk of flooding. More precisely, a two-third of water produced due to HOR was transported to cathode during the cell operation which is more than the amount of water consumed at the cathode. Further the water content measured at both anode and cathode outlet gas streams (using humidity sensor) was much more elevated than that at inlets emphasizing that the limiting factor was not cathode dry out but flooding. These conclusions may not be generalized as the experimental and theoretical values are considered for Tokuyama A201 membrane only hence further investigation are needed.

M.R. Gerhardt *et al.* [147] developed a model to quantify the effect of membrane hydration on local current density. At the channel beginning a significant overpotential is observed due to Ohmic resistance of membrane. However, the Ohmic resistance down the channel was reduced due to an improved liquid saturation by HOR. Once the anode reaches saturation humidity level, a water concentration gradient is developed between anode and cathode resulting in water transport through the membrane. At 50 % RH of inlet gases, a water flux ratio (back diffusion flux / produced flux) of 0.5 indicates that enough water is transported from anode to cathode and beyond this value, this leads to cathode flooding. The water flux in turn depends on the diffusion coefficient of the membrane. A 10 times decrease in diffusion coefficient of a Tokuma A 201 membrane resulted in water starvation at cathode while a 10 times increase in diffusion coefficient resulted in flooding of cathode. From these simulated results one can conclude that, the diffusion coefficient has significant influence on water transport properties of AEMs and an optimization of the diffusion resistance (membrane

thickness/diffusion coefficient) is desirable to maintain adequate liquid saturation at cathode of AEMFC.

We can notice that very little data is reported in the literature about the sorption [148–151] and diffusion of water [151] in alkaline membranes and about the electro-osmotic drag coefficient [151,152]. Characterization work on the water transport properties will have to be carried out in the same way as what was done for Nafion. Finally, one should pay careful attention towards hydrophilic and hydrophobic properties, thickness and diffusion resistance of AEM to eliminate water imbalance through AEMs.

3.2 Operating conditions

3.2.1 Effect of relative humidity

Reactant gases are generally humidified before they are fed to respective electrodes to supply water to the cell [153]. Although there are numerous ways to humidify the cell but still bubble humidifier (passing the reactant gases through a hot water bath before they reach the inlet of the cell) is predominantly used for research purpose due its simple operation. Unlike in PEMFC humidification is required only to hydrate the membrane while in AEMFC humidification is necessary to hydrate the AEM and to provide adequate water for ORR at the cathode [154]. Hence selecting a proper humidification strategy is a key to achieve desired performance in AEMFC. A part of water carried to cathode is being utilized in ORR, transported electro osmotically to anode and the excess water is removed through gas exhaust. Similarly, water brought by anode gas stream is partially transported to cathode through back diffusion and the excess of water is drained by gas exhaust. Although, it is believed that operating AEMFC at high RH facilitates OH^- conduction reducing Ohmic losses and mitigates cathode mass transport losses [155], the optimal gas humidification strategy depends on several operating parameters such as current density, temperature, stoichiometry and pressure [156].

T.J. Omasta *et al.* [58] proved that better AEMFC performance could be achieved with partially humidified gases (87/79 %) rather than fully humidified gases using GDLs with 0 % PTFE.

It is also interesting to study the effect of RH of anode and cathode gas feeds separately as the former produces water and the later one consumes water. Although water is generated at the anode due to HOR, humidification of anode inlet is necessary as there is a significant amount of water loss due to back diffusion and evaporation [157]. Huo *et al.* [156] deduced from a modelling study that the effects of RH of cathode and anode gas streams are similar. K. Jiao *et al.* claimed that water accumulation at the anode in liquid form was possible with fully humidified inlet gas feed, while gas feed with partial humidification resulted in vapor water which could be removed easily; more precisely the liquid water volume fraction at anode was increased from 0 to 0.11 after changing the anode inlet RH from 90 to 100 %. [141]. Y.-J. Sohn *et al.* simulation studies further revealed that anode humidification was crucial for optimum AEMFC performance [158]. They observed only marginal loss in performance when AEMFC was simulated with dry cathode and fully humidified anode while dry anode and fully humidified cathode showed a significant loss in performance. This can be explained by the higher diffusion coefficient of water vapor in hydrogen compared with diffusion of water vapor in oxygen or air. A dry hydrogen flow rate would dry the AEM more easily than a dry air flow rate. The importance of anode gas RH was also justified by T. Wang *et al.* in their experimental work [159]. They adopted a straightforward method of over saturating the cathode gas stream and varied anode gas RH. The optimum RH at anode side was reported as 80 % below which there was significant elevation in area specific resistance (ASR) (50 mΩ/cm² at 80% RH and 59 mΩ/cm² at 70 % RH) owing to dehydration of AEM. On the upper side, when the anode RH reached 95 %, the cell stopped working; even at 93 % there existed significant flooding at low current density. The good water management of the cell is also shown by the polarization curves taken under forward and reverse scan. It is a general hypothesis regarding water management

of the cell that a cell with proper water management shows no deviation between forward and reverse scan and the polarization curves overlap each other. From T. Wang *et al.*, the polarization curves taken in reverse scan was well fitted with that taken under forward scan at 80 % inlet anode RH validating the above hypothesis.

AEMFC performance is also sensitive to RH of cathode gas stream as there is significant amount of water loss due to electroosmotic drag and water consumption during ORR. Thus cathode gas stream with high RH is suggested. D.R. Dekel *et al.* model predicted that AEMFC operating at 0.5 A/cm^2 showed a 100 mV increase in cell voltage when the RH of cathode gas feed was changed from 25 to 100 % and this increase in cell voltage was more pronounced at higher current densities [160]. Nevertheless, before optimizing the RH of cathode gas feed one has to consider the amount of water transported from anode to cathode by back diffusion. If the water transport resistance from anode to cathode is higher (AEMs with low water diffusion, thicker AEM), then the cathode gas feed with high RH is preferred to counteract the water loss during ORR and electroosmosis. If there is no back diffusion or under extremely low back diffusion, injection of liquid water to cathode flow channel was considered to satisfy the cathode water demand. K. Jiao *et al.* reported that injection of extra liquid water at cathode with a volume fraction of 0.08 (100 % RH +0.08 liquid) could significantly enhance the AEMFC performance, however the effect was insignificant at higher temperatures (60 °C) [161]. Another model developed by S. Huo *et al.* considering the injection of liquid water with volume fraction of 0.2 showed a 100 % increase in achievable power compared to 60 % RH [65]. However, injection of liquid water may cause flooding in CL, hence further experimental study is rather important to establish this proposal.

As consumption and production rates of water vary according to the operational current, one should tune the RH accordingly [153]. At high current densities low RH hydrogen feed is necessary to avoid anode flooding as water production is quite rapid. Figure 8 shows the spatial distribution of water within the anode and the cathode as function of inlet RH and cell voltage.

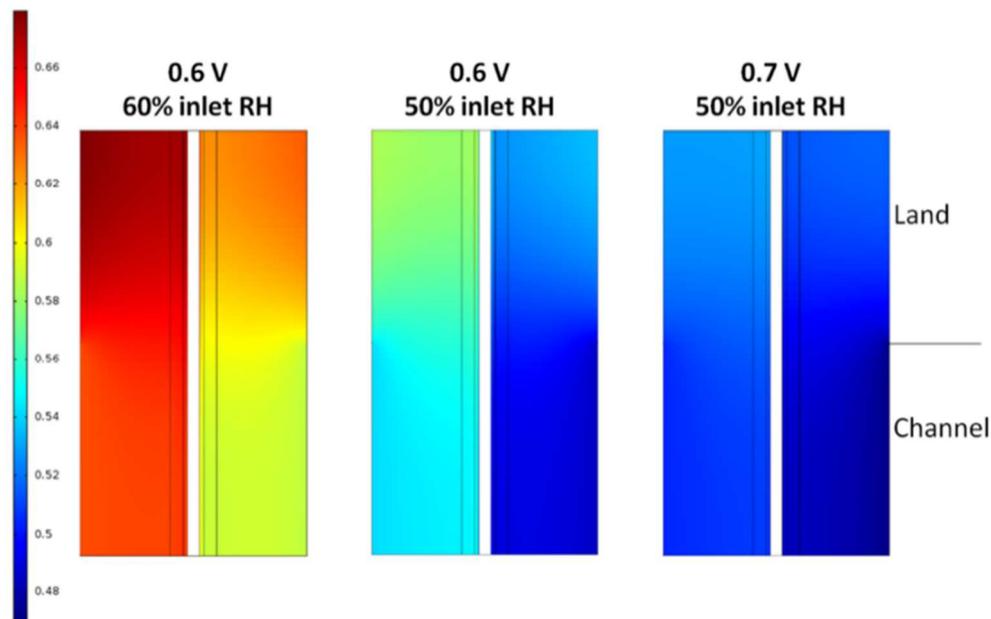


Figure 8. Spatial distribution of water in anode (left side) and cathode (right side) with respect to voltage and RH of inlet gas. Reproduced with permission from Ref. [153].

The anode shows more water content than the cathode in all the used conditions as expected and consistent with the fact that water is produced at the anode and consumed at the cathode. It is interesting to see that the RH is not uniform and higher under the land than the channel because of temperature heterogeneities.

On the other hand, M.R. Gerhardt *et al.* computational model revealed the effect of humidification on the local current density [147]. At low humidification, the channels near the inlet experience dried out and showed low current values while the maximum current was seen at the position near the outlet. In contrast, at high RH, the scenario was reversed showing high

current near the inlet and low current at the exit due to flooding effect, meaning that the position peak current varied as a function of inlet gas humidification. Some experiments using a segmented cell would be interesting for validating these simulation conclusions [42].

At the end, taking into account that both membrane and ionomer are not stable under dry conditions, it might be interesting to humidify the gases a little more than necessary; such approach would lead to electrical performance reduction and durability improvement [8].

3.2.2 Inlet gas flow

As described above, the AEMFC anode is fed with hydrogen and the cathode is fed with oxygen or air according a certain stoichiometric ratio. Generally, gases are supplied to the electrodes at a much higher amount than what it is really consumed in the reaction to maintain the homogeneous distribution along the channels and to push the excess water out from the CL[58]. It is believed that the higher flow rate of inlet gas helps to drag the liquid water across the flow channel maintaining a uniform liquid atmosphere at the channel|GDL interface. Since the AEMFC anode is in water-rich atmosphere, it is interesting to see the cell performance as function of the anode flow rate. The simulation and experimental results revealed that the increased anode flow rate has a positive effect on the cell performance particularly at high current densities at which excess of water is removed more efficiently through gas exhaust. Y. Oshiba *et al.* [143] demonstrated that at high potential, changing anode flow rate from 100 to 1000 mL/min had only a minimal effect on the performances while at low potential, the current density of the cell operating at 100 % RH was increased from 100 to 800 mA/cm² due to mitigation in anode flooding. On the other hand, T.J. Omasta *et al.*[58] studies revealed 60 % decrease in cell performance when the flow rates of both hydrogen and oxygen were reduced from 1000 to 750 mL/min due to CL flooding. It is to be noted that the decrease in performance could only be attributed to cathode mass transport losses as there was no significant difference observed when only anode flow was reduced to 200 mL/min. This is further explained by

lowering reactant supply to cathode by a factor of 5 (replacing O₂ with CO₂ free air) which showed only 10 % drop in peak power which proves that volumetric flow rate had significant effect on managing the cathode water. These results are also in accordance with M. R. Gerhardt *et al.* modeling study in which they observed that increasing cathode gas flow alleviated the cell performances due to reduced mass transport losses [147]. However high flowrate demands thicker AEMs as thinner membranes have high gas permeability leading to cross-flow causing mixed potentials at the anode and/or the cathode which leads to failure of the cell [162]. Hence it is important to achieve a good balance between the flow rate of inlet gases and membrane gas permeability.

Along with the flow rate, the flow direction also deserves a significant consideration, for example counter-flow (anode gas and cathode gas flow in opposite direction) improves the current density at the entrance of the cathode compared to co-flow (anode gas and cathode gas flow in the same direction). AEMFC operating in counter flow mode allows water to transport from anode outlet to cathode inlet maintaining adequate hydration at the inlet of cathode, meaning to say that the direction of flow affects the distribution of local current density along the channels. However, the average current density obtained in co-flow and counter-flow methods does not vary much but the local current density does vary [147] and is further supported by B. S. Machado *et al.* [163]. In their study wherein they pointed out that flow direction had minimum impact on overall current density as the supply of the reactants was not affected by the direction of flow but the counter-flow configuration at cathode could enhance the liquid water drag from anode to cathode. Such configuration was beneficial to lower anode flooding and similar effect was also observed in PEMFC [164].

In addition, applying a back pressure is another strategy to manage water in the cell and to improve the reactant transport to the electrode surface. Generally, equal backpressure is applied at both anode and cathode to avoid any physical damage to the membrane. However,

mechanically robust AEMs give raise a possibility to apply different pressure at anode and cathode. This unequal backpressure is beneficial as the anode requires drain the excess water and cathode require to retard water. H. Deng *et al.* modelling study predicted that applying backpressure at anode side could be beneficial to control the flooding. They proposed that water transport from anode to cathode could be improved through the AEM by hydraulic permeation, this would lead to adequate water at the cathode for consumption during ORR and for AEM hydration. Figure 9 shows the distribution of RH at cathode as function of anode back pressure [66]. It is to be noted that, as the anode back pressure increases, liquid saturation in CCL is improved due to depression in water transport through electroosmosis and subsequent improvement in hydraulic permeation. For example, at 6000 Pa of anode gas, RH of CCL reached above 90 % which will help to mitigate Ohmic losses and facilitate adequate water amount for ORR.

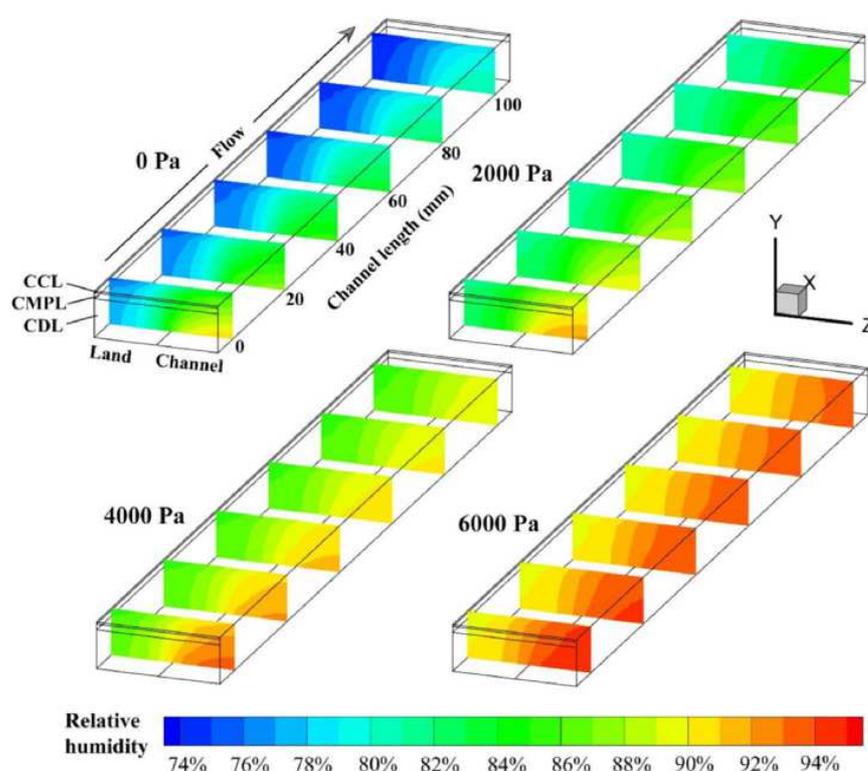


Figure 9. Effect of cathode RH as the function of anode inlet back pressure operating at 40 °C under constant voltage of 0.5 V (CCL: cathode catalyst layer; CDL: cathode diffusion layer; CMPL: cathode micro porous layer). Reproduced with permission from Ref. [66].

In contrast, T. Wang *et al.* proposed in their experimental study that high back pressure on the anode side could be unfavorable as it would improve the water retention and decrease the evaporation by improving the boiling point of water under high partial pressure[159]. Nevertheless, applying high back pressure at cathode would be beneficial to retain water at cathode and improve oxygen transport. This hypothesis was demonstrated by recording the polarization curves in two different cases *i.e.* at a backpressure of 250 kPa on both sides and 125 kPa on the anode side and 250 kPa on the cathode side. Among these two cases, the reduced back pressure at anode side showed better and stable cell performance attributing the better water management.

3.2.3 Effect of temperature

The effect of the operating temperature on the cell performance cannot be overlooked as it has an active role to eliminate excess of water in CL and GDLs through evaporation. Further, increase in operating temperature improves the electrochemical kinetics and membrane hydration ultimately delivering higher mean current density for a given voltage [151]. Generally, AEMFC is operated at ≤ 60 °C beyond which AEM and ionomer materials are prone to degradation. However, some simulation and experimental studies were conducted to explore insights of the temperature effect. The results revealed that operation at higher temperature (around 70 °C) leads to improve the cell performances. M. Iravaninia *et al.* observed 43 % of increase in power density when they increase the temperature of the cell from 40 to 60 °C at 100 % RH using quaternized poly sulfone based AEM (Figure 10) [88]. This beneficial effect was attributed to enhanced electrode kinetics and ionic conductivity and better transport through the AEM. In an experimental study, T.J. Omasta *et al.* demonstrated that the AEMFC power density could be improved up to 100 mW/cm² by increasing the cell temperature from 60 to 70 °C due to delayed mass transport limitations (from 0.6 to 0.2 V) [58]. Similarly V.M. Truong *et al.* [57] work also proved that AEMFC operated using a commercial AEM based on quaternary

ammonium polysulfone (AT-1 supplied by Hephass Energy Co., Ltd) delivered 22 % increase (from 500 to 610 mWcm²) in power density as a consequence of a 10 °C rise in cell temperature (from 60 to 70 °C).

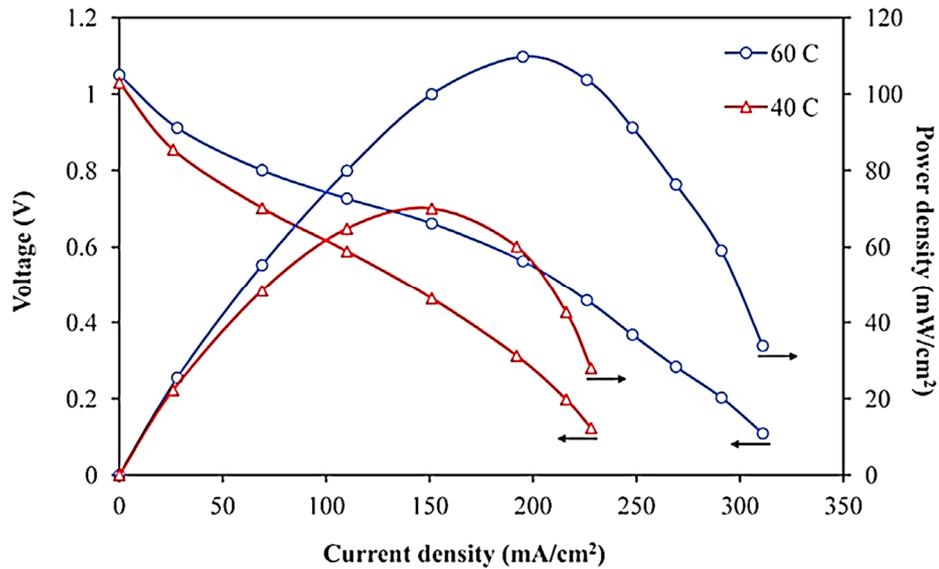


Figure 10. Effect of the temperature on AEMFC performance using quaternized poly sulfone based AEM (Pt loading 0.5 mg/cm² on both anode and cathode). Reproduced with permission from Ref. [88]

However, the observed performance enhancement is attributed not only to improved electrode kinetics and enhanced ionic conductivity of AEM [165] but it is also due to better water management of GDLs. As temperature increases, the water vapor saturation pressure gradient through the GDL increases too much leading to a higher diffusive water vapor flux, cleaning the pores from liquid water and clearing the path for reactant supply to CLs. Nevertheless, it is rare to find AEMFC investigations above 60 °C as most of the AEMs are unstable at the temperature 60 °C. The recent targets of AEMFC given by US department of energy (DOE) revealed that AEMFC should be operated above 60°C to improve the electrode kinetics [166]. Although there are few membranes based radiation-grafting onto poly(ethylene

co-tetrafluoroethylene) (ETFE) [28], quaternary ammonia polysulfone [167], quaternized poly(2,6-dimethyl phenylene oxide) (QAPPO) [168] reported to be stable up to 80 °C, AEMFC data of such membranes is not available. Hence, ongoing efforts are being made in polymer chemistry to develop sustainable AEMs at high temperature.

4. Conclusions and future prospective

Water management across various parts of AEMFC is critical to achieve high performance, it is believed that developing high hydroxyl ion-conducting, durable AEM is the limiting factor of AEMFC to compete with PEMFC. However, the recent studies showed significant progress in AEMs and they proved that the bottle neck is no longer an AEM but the effective water management. Thanks to AEM research community, at least there are few reference membranes such as FAA-3 (Fuma-Tech), Tokuyama A201. Other start-ups like Dioxide materials, Xergy, Orion and Ionomer are also promising commercial suppliers of AEMs and ionomers. As far as GDL is concerned, inclusion of MPL at the anode seems to be beneficial to minimize the flooding. PTFE content in MPL was optimized without affecting the porosity and electronic conductivity. Selecting suitable ionomer and catalyst loading is another crucial pointed. One should keep in mind that optimized electrodes must have appropriate thickness, hydrophobicity, porosity and ionic/electronic conductivities. Adequate ionic contact with the membrane must also be ensured. AEMs with high water diffusion rate are beneficial as they transport excess of water from anode to cathode to maintain uniform hydration across the cell providing sufficient water for ORR. However too much diffusion may cause cathode flooding. It is hence important to establish an equilibrium between water consumption at the cathode and diffusion rate. Inlet RH of gases plays a vital role to optimize the cell water as it carries water vapor to cell. Nevertheless, selecting ideal RH depends on various parameters such as electrodes' hydrophobicity, membrane diffusion properties, water production rate at anode and consumption rate at the cathode.

In spite of numerous efforts, stable AEMFC performance was not achieved yet due to significant knowledge gap in the operational parameters of AEMFC. However, in recent literature, it was reported that the achievable power density can be 2-3 W/cm². With non Pt group catalyst the achievable performance was reported as high as 1 W/cm² emphasizing that AEMFC is no longer inferior to PEMFC technology. There is huge potential in the research areas of non-Pt catalysts and stable electrolytes with high conductivity and stability. Operating conditions of AEMFC is one critical research area to explore and manage water for each of the component, which is crucial for stable performance of AEMFCs. Further experimental, theoretical and combined simulation/experimental studies are of great important to modify the existing systems to manage the water much more effectively. The key water management strategy to be followed are: (i) optimizing the hydrophilic/hydrophobicity of electrodes, (ii) optimizing of Pt loading and ionomer in the catalyst layer to yield maximum electrochemical active surface area, (ii) employing thin and robust AEMs to reduce ohmic resistance and water diffusion resistance. Alkaline environment is beneficial in the stability point of view, but in reality life time of AEMFC was demonstrated as few hundred hours and is not sufficient in commercialization prospective which is why delivering continuous power for commercial applications has not been realized. Thus, to realize the potential of anionic membrane fuel cells, research needs to be conducted on materials and system management strategies. With respect to materials, more chemically and mechanically resistant membranes and ionomers need to be designed. Highly hydrophobic electrodes should be designed using preferably non-carbon catalyst supports to avoid the production of carbonates which reduces ionic conductivity.

New system management strategies also to be proposed in order to optimize water management in particular. This can be done by favoring certain temperature gradients that drives the transfer of water in vapor form. As long as the catalyst supports are carbon species, care must be taken to limit the potential of the cathode to ensure that carbonates are not formed. It is at the cost of

this research efforts at the materials and systems levels that AEMFC will achieve to supplant PEMFC.

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