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Importance of balancing membrane and electrode water in anion exchange membrane fuel cells

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HIGHLIGHTS

- Very high power density achieved, 1.4 W cm^{-2} at 60°C .
- Water content and balance play significant role in AEMFC performance.
- Electrode and operational variable investigated.
- Anode and Cathode flooding observed under certain conditions.
- High conductivity membranes enable rapid water back diffusion.

GRAPHICAL ABSTRACT

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ABSTRACT

Anion exchange membrane fuel cells (AEMFCs) offer several potential advantages over proton exchange membrane fuel cells (PEMFCs), most notably to overcome the cost barrier that has slowed the growth and large scale implementation of fuel cells for transportation. However, limitations in performance have held back AEMFCs, specifically in the areas of stability, carbonation, and maximum achievable current and power densities. In order for AEMFCs to contend with PEMFCs for market viability, it is necessary to realize a competitive cell performance. This work demonstrates a new benchmark for a H_2/O_2 AEMFC with a peak power density of 1.4 W cm^{-2} at 60°C . This was accomplished by taking a more precise look at balancing necessary membrane hydration while preventing electrode flooding, which somewhat surprisingly can occur both at the anode and the cathode. Specifically, radiation-grafted ETFE-based anion exchange membranes and anion exchange ionomer powder, functionalized with benchmark benzyltrimethylammonium groups, were utilized to examine the effects of the following parameters on AEMFC performance: feed gas flow rate, the use of hydrophobic vs. hydrophilic gas diffusion layers, and gas feed dew points.

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1. Introduction

Anion exchange membrane fuel cells (AEMFCs) have

experienced a surge of interest in the past decade as a lower cost alternative to proton exchange membrane fuel cells (PEMFCs) [1–3]. The increased pH in the alkaline AEMFC facilitates the use of a wider range of non-precious metal catalysts at the cathode due to favorable oxygen reduction reaction kinetics in alkaline vs. acid media [4,5]. Anion exchange membranes (AEMs) have also demonstrated a lower fuel permeability than proton exchange

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membranes when used in direct alcohol fuel cells [6]. Additionally, switching to AEMFCs enables the use of lower cost cell and stack components because of increased materials stability in alkaline vs. acidic environment. Despite these significant advantages, PEMFCs have remained favored due to a sizable performance gap between the two technologies [1,7–11]. Recently, this situation has improved [12–14], but the level of understanding on what factors are important for improved performance is still limited. Therefore, further studies are required to fully understand the fundamental and operational variables that limit AEMFC performance, and to develop strategies that overcome these limitations.

One variable that has been mostly overlooked in the AEMFC literature is the cell water content and balance. This is most likely because of the differences in the role of water in AEMFCs (Fig. 1A) vs. PEMFCs (Fig. 1B). In PEMFCs, water is only generated (at the cathode as a product of the oxygen reduction reaction, ORR) and not electrochemically consumed, such that its major role is the hydration of polymer electrolyte components to facilitate H^+ conduction. Water is also moved to the cathode from the anode by electro-osmotic drag as H^+ produced by the hydrogen oxidation reaction (HOR) moves through the PEM. Thus, removing cathode water is the prime concern in the PEMFC to avoid catastrophic electrode flooding. Though it is possible at high current densities to dry out the PEMFC anode, the high rate of water back diffusion through Nafion® (especially thin *ca.* 25 μm membranes) can naturally mitigate against this effect.

In the AEMFC, water is both electrochemically generated (at the anode from the HOR) and consumed (at the cathode by the ORR) during cell operation. Water is moved from the cathode to the anode by electro-osmotic drag (in the reverse direction of a PEMFC). There is a need in this system to provide adequate water to maintain AEM and electrode hydration, without flooding or drying out the catalyst or gas diffusion layers [15] – both of which can limit the achievable current and power densities of operating cells. The challenge faced is that the balance between proper membrane hydration and flooded catalysts layers is thin, which can lead to low performing cells that are the result of undiagnosed water management issues, not the cell components used (*i.e.* catalysts, membrane). At one extreme, excess water in the catalyst layers can lead to catastrophic flooding. At the other, it is becoming apparent

that OH^- -derived AEM degradation is most serious at low hydration (typically at the cathode) [16].

The properties of specific AEMs influence not only primary water behavior, *i.e.* number of molecules of H_2O per stationary cation(+) site (λ), ion exchange capacity (IEC), and conductivity (σ), but also secondary effects such as water back diffusion (anode to cathode). To avoid cathode dry-out and/or anode flooding in AEMFCs, it would be preferable for the AEM to have high water back diffusion. However, many AEMs in the literature do not have the same efficient phase separation as Nafion® and limited OH^- conductivity (Table 1), which translates directly to low water back-diffusion rates [15,17]. Therefore, engineering solutions have been explored in a number of studies, including running commercial systems at very low current density [16], pressurizing the gas streams, or even feeding condensed water through the cathode [10] – none of which are tenable long-term solutions to high performing AEMFCs. Compared to many modern AEMs (Table 1), radiation-grafted ETFE-based AEMs have been reported to have high conductivity [13,18] and high water back diffusion rates [15,17], which may be utilized to alleviate the water gradient that is intrinsic to operating AEMFCs. However, high water back diffusion risks the introduction of new variables to be considered, including the possibility for cathode flooding.

The aim of this work is to examine the influence of the electrode and gas diffusion layers as well as the flow rate and dew points of the anode and cathode gases on AEMFC performance. ETFE-based benzyltrimethylammonium-functionalized radiation-grafted alkaline AEMs and anion exchange ionomers (AEIs) are investigated [9]. In order to maximize cell performance, both hydrophobic and hydrophilic gas diffusion layers are tested, which when coupled with manipulation of the gas feed dew points (from water poor to water rich conditions) allows for a better understanding of how to maintain AEM and AEI hydration without flooding the catalyst layer.

2. Experimental

2.1. AEM synthesis and characterization

ETFE film (25 μm thickness) was supplied by Nowofol

Fig. 1. Schematic comparison of water consumption, generation, migration, and diffusion in AEMFCs (A) and PEMFCs (B).

Table 1

Selected high peak power density and conductivity AEMs in the literature.

AEM Chemistry	Peak Power Density W cm ⁻²	Cell Temp °C	A/C Dew Points °C	Back Pressure kPa _g	Conductivity (OH ⁻), σ , mS cm ⁻¹	Ex-situ σ Condition °C/RH
ETFE-g-VBCTMA [this work]	1.40	60	54/57	0	132	80/95%
aQAPS [14,19]	1.00	60	60/60	100	108	80/100%
LDPE-g-VBC [11]	0.82	60	70/-	0	100	60/100%
A901 [10]	0.74	80	85/85	250	38	20/90%
BPI (74.6% DOG) [20]	0.61	50	—	0	105	60/100%
PF AEM Gen 1 [21]	0.43	60	60/60	—	55	23/100%
MHT-PMBI [22]	0.37	60	60/60	0	23	30/95%
T25NC6NC5N [23]	0.36	60	60/60	100	99	23/100%
PVBTA [24,25]	0.28	60	52/59	—	91	80/90%
C-HPPEs-4/1 [26]	0.08	80	80/80	—	77	30/100%

- not reported.

Kunststoffprodukte GmbH (Germany). VBC monomer (mixture of 3- and 4-isomers; 500–100 ppm *tert*-4-butylcatechol and 700–1100 ppm nitromethane inhibitors) was supplied by Sigma-Aldrich and used without the removal of inhibitors. 1-Octyl-2-pyrrolidone and aqueous trimethylamine solution (TMA, 45 wt%) were also purchased from Sigma-Aldrich. Toluene and 2-propanol were of reagent grade and supplied by Fisher Scientific. All chemicals were used as received. The ultra-pure deionized (DI) water used in this work had a resistivity of 18.2 M Ω cm.

The AEM was prepared from pre-formed ETFE films using the peroxidation (pre-irradiation in air) method previously reported [12]. The ETFE films were subjected to electron-beam irradiation in air to 30 kGy total absorbed dose (using a 4.5 MeV Dynamatron Continuous Electron Beam Unit at Synergy Health, South Marston, UK). As the irradiation step is performed in air, immediate reaction of the radicals that are formed with O₂ molecules leads to the creation of peroxide and hydroperoxide groups on the polymers. The peroxidated ETFE films then act as a solid-state free-radical initiator for the subsequent graft polymerization step. After irradiation, the films were transported back to the laboratory in dry ice before they were stored in a freezer at -40 °C (the peroxide groups are stable for around 6 months at this temperature [27]).

For the grafting step, the electron-beamed films (15 cm × 15 cm) were immersed in an aqueous dispersion of VBC (5%vol.) in sealed vessels along with addition of dispersant (1%vol. 1-octyl-2-pyrrolidone). The solutions were purged with N₂ for 2 h before the vessel was sealed and heated at 70 °C. After the reaction period, the films were removed from the grafting mixture and washed in toluene; this process is employed to remove excess unreacted VBC and any poly(VBC) homopolymer (not bound to the ETFE base material) that may be present. The resulting intermediate ETFE-g-poly(VBC) films were subsequently dried at 70 °C for 5 h in a vacuum oven to remove all traces of solvent. The gravimetric degree of grafting (DoG, %) of the intermediate membranes was calculated using Equation (1).

$$\text{DoG} = \frac{m_g - m_i}{m_i} \times 100\% \quad (1)$$

where m_g is the mass of the grafted sample and m_i is the initial mass of the pre-grafted irradiated films.

To quaternize, the intermediate films were then submerged in the aqueous TMA solution at ambient temperature for 24 h, then washed in DI water, and finally heated in fresh DI water; this procedure was adopted to remove any excess TMA from the resulting quaternized ETFE-g-poly(vinylbenzyltrimethylammonium) AEMs. Final conversion to the chloride-anion-form ETFE-g-poly(-VBTA⁺Cl⁻) AEMs was achieved by immersing the AEMs in aqueous NaCl (1 M) for 15 h with one change of NaCl solution

during this period to ensure complete ion-exchange. The resulting AEMs were then soaked in deionized water to remove any excess NaCl-derived co- and counter-ions. The final desired radiation-grafted AEM(Cl⁻) films were stored in water until required and were not allowed to dry out at any point before subsequent measurements/experiments were conducted.

Table 2 summarizes the key properties of the AEM films used in this study. Details on the standard methods to characterize the AEM, such as ion-exchange capacity (IEC), water uptake (WU), through plane swelling (TPS), and conductivity determinations, can be found in our recent synthesis optimization study [12].

2.2. Anion-exchange ionomer (AEI) powder synthesis

The synthesis of the AEI powder was reported previously [9] and is summarized here. ETFE powder (Z8820X, AGC Chemicals Europe) with a particle size of 20–30 μ m was peroxidated in air using an electron-beam with a total absorbed dose of 70 kGy. The resulting “activated” powder was then submerged in a solution containing VBC, 2-propanol, and Surfadone LP-100 (ISPcorp) with a volume ratio of 1.00:3.95:0.05. The mixture was purged with N₂ for 2 h, and then sealed and heated for 72 h at 60 °C. The powder was recovered by filtration, washed with toluene, and dried at 50 °C under vacuum, resulting in ETFE-g-poly(VBC) grafted powders.

The powder was quaternized by submersion in an aqueous TMA solution (TMA, 50%wt. in water, Acros Organics) for 5 h at ambient temperature. The resulting powder was washed 5 times with DI water, and then heated in DI water for 18 h at 50 °C. After a further water wash step (5 × DI water), the powder was dried for 5 d at 40 °C under vacuum. The final resulting ETFE-g-poly(VBTMA⁺Cl⁻) AEI powder (in the most chemically stable Cl⁻ form), that was used in all of the electrodes in this manuscript, possessed an IEC of 1.24 ± 0.06 mmol g⁻¹ ($n = 3$).

2.3. Materials and gas diffusion electrode (GDE) preparation

First, the AEI powder was ground with a mortar and pestle for 10 min to reduce the amount of aggregated particles. Next, 100–150 mg of one of three carbon supported catalysts was added to the AEI in a 20:80 (AEI:catalyst) mass ratio along with 1 mL DI water: BASF C1-50 (50%wt. high purity Pt supported on Vulcan XC-72R carbon), Alfa Aesar HiSPEC 4000 (Pt, nominally 40%wt., supported on Vulcan XC-72R carbon), or Alfa Aesar HiSPEC 10000 (Pt, nominally 40%wt., and Ru, nominally 20%wt., supported on Vulcan XC-72R carbon). Each catalyst-AEI mixture was ground with a mortar and pestle for 10 min, a length of time that was selected because it invariably produced a visually and texturally homogeneous slurry, suggesting that no AEI agglomerates remained. Then, 2 mL of 2-propanol (Fisher Chemical Optima) was added to the

Table 2Summary of the key properties the AEM used in this study. Errors are sample standard deviations (repeat measurements on $n = 3$ samples of the AEM).

AEM	DoG (%)	IEC Mmol g ⁻¹	WU (%)	T _{dry} μm	T _{hyd} Mm	TPS (%)	σ _(Cl⁻ 80 °C) mS cm ⁻¹
RG-ETFE(30 kGy)-AEM	79	2.05 ± 0.05	67 ± 7	45 ± 2	60 ± 1	33 ± 4	63 ± 2

mortar and ground for a further 5 min, after which the catalyst slurry was completely transferred to a LDPE vial, and combined with an additional 7 mL of 2-propanol to produce a low viscosity ink. Each ink was homogenized in an ambient temperature ultrasonic bath (Fisher Scientific FS30H) for 60 min, during which time the water in the ultrasonic bath was replaced three times to avoid overheating.

The resulting catalyst inks were used to fabricate gas diffusion electrodes (GDEs) by hand spraying onto a larger area gas diffusion layer (GDL) with an Iwata Eclipse HP-CS using 15 psig N₂ (Airgas Ultra High Purity). The GDLs used were Toray TGP-H-060 with either 5% PTFE wetproofing or 0% PTFE wetproofing by weight. 5 cm² GDEs were then cut from the larger sprayed electrode for use in the cell hardware. Generally, the target total metal loading of the resulting GDEs was 0.6 ± 0.1 mg_{metal} cm⁻², and the actual catalyst loading for each data set will be given in the text and/or figure captions.

2.4. MEA assembly and single-cell AEMFC testing

Prior to MEA and fuel cell assembly, the GDEs and AEMs were separately immersed in aqueous KOH (1 M, Fisher Chemical, pellets/certified ACS) for 60 min, replacing the solution every 20 min to ensure complete ion-exchange. During this hydration and ion-exchange process, no substantial electrocatalyst or AEI particles were observed to wash off the GDE surface, showing adequate adhesion of the catalyst layers onto the GDLs. Excess aqueous KOH and water were removed from the electrodes and membrane with a laboratory cloth prior to assembly. Each set of GDEs and AEM were pressed together in-cell to form the membrane electrode assembly (MEA) with no prior hot pressing. The MEAs were secured in 5 cm² Fuel Cell Technologies hardware between two single pass serpentine flow graphite plates using 6 mil (150 μm) PTFE gaskets with 20% pinch (5.1 N m torque). An 850E Scribner Fuel Cell Test Station was used for all testing. H₂ and O₂ gas feeds were supplied to the anode and cathode, respectively, at various flow rates and dew points without back-pressurization (*ca.* 1 atm absolute). Throughout this manuscript, the dew points of the supplied gases will be identified in an *Anode/Cathode* format with the dew points reported in °C, *e.g.* 57/55 would correspond to an anode dew point of 57 °C and a cathode dew point of 55 °C. The cell temperature was held constant at 60 °C ± 0.5 °C for a majority of the experiments. In the cases where cell temperatures other than 60 °C were used, the reported format will be *Anode/Cathode/Cell* in °C, *i.e.* 69.5/69.5/70 for a cell operating at 70 °C with symmetric feed gas dew points slightly below saturation. The temperature of the heated gas follow lines between the fuel cell test stand and the cell were maintained at 5 °C above the respective gas dew points.

All of the polarization curves shown were collected under potentiometric control at a scan rate of 10 mV s⁻¹ in order to better tease out flooding issues under water starved and flooded conditions. When the water management issues were well controlled, there was not a significant difference between point by point and linear sweep polarization curves, which is shown in Fig. S1 for the highest performing cells. Additionally, tests were repeated after multiple hours and varying the testing conditions to ensure stability, recoverability, and repeatability.

3. Results and discussion

3.1. Cell operation and response during start-up/break-in

The typical startup procedure for AEMFCs is simple and comparable to PEMFCs [8,28,29], where a constant cell discharge voltage is controlled for a set time [12,30]. In AEMFCs, the startup procedure does two things: (1) similar to PEMFCs, hydration and formation of ion transport domains throughout the membrane; and (2) allows for the purging of (bi)carbonate (CO₃²⁻ and HCO₃⁻) ions from the MEA (formed on exposure of the OH⁻-exchanged MEA components to CO₂ in the air on transfer to the fuel cell test fixture). The latter activation process lowers the ohmic resistance of the cell by ensuring the anion transport is predominantly OH⁻ [31]. To control the charge mobility and (bi)carbonate removal (independently to some extent), this work employs a two-stage break-in procedure, starting at a “low strain” with a voltage hold at 0.5 V, followed by a more aggressive, brief voltage hold at 0.2 V. The separation of these two steps is intended to maximize membrane performance by avoiding the use of a long duration, high current stress that could accelerate membrane degradation [16,30,32].

During the first break-in stage at 0.5 V, a cell will typically show a steady current increase over time until a preliminary plateau is reached (typically after 40–60 min). At this point, the cell is moved to the second break-in stage at 0.2 V. Under control at 0.2 V, the cell will undergo a further increase in current as (bi)carbonate anions are removed, along with additional water being driven through the AEM by electroosmotic drag. As the (bi)carbonate anions are purged from the AEM, they are expelled as CO₂ in the anode exhaust as (bi)carbonate participates in the HOR [33].

At full gas humidity, *i.e.* 60/60, the transition from 0.5 V to 0.2 V can be problematic as the increase in current disrupts the water balance, resulting in an instability in the voltage and current outputs of the cell. A more subtle example of this issue can be observed in Fig. 2A where the voltage and current are unstable for the first 2.5 min of the second (0.2 V) break-in stage. The current increases significantly during this voltage instability, from 1.3 to 1.8 A cm⁻². After the voltage stabilizes, the current further increases and peaks at 2.1 A cm⁻² before starting to decline. The increase in cell current to 2.1 A cm⁻² coupled with the change in cell potential facilitates the “self-purging” phenomena that is known to occur through an increased generation of OH⁻ at the cathode and flux of OH⁻ ions to the anode [1,31,34]. The (bi)carbonate self-purging during startup was observed by passing the anode effluent through a non-dispersive infrared CO₂ detector (PP Systems SBA-5). While some CO₂ is detected when the cell is held at 0.5 V, a significant amount of CO₂ elutes when the cell is polarized to 0.2 V, as expected. These spikes in the effluent CO₂ correspond to the self-purging of (bi) carbonates associated with the covalently-bound cations on the AEM and AEI polymeric chains and in the accompanying water phase (ion displacement and a shift in OH⁻/(bi)carbonate equilibrium).

Fig. 2B depicts a startup with more significant water management challenges: the current increase is low during the initial 0.5 V hold, and the cell is extremely unstable when the polarization is increased to 0.2 V, which results in a complete cell “crash”. This erratic behavior is a well-known characteristic of electrode flooding

Fig. 2. Performance data for cell startup and the effects of humidity. Cell Temperature was 60 °C with a 1.0 L min⁻¹ flow rate of H₂ and O₂ at the anode and cathode, respectively. (A) Cell startup with minor problems (Anode: 0.69 mg_{PtRu} cm⁻² on 5% PTFE, Cathode 0.35 mg_{Pt} cm⁻² (Alfa Pt/C 40%wt) on 0% PTFE GDL, dew points 60/60); (B) Startup with major flooding (Anode: 0.35 mg_{PtRu} cm⁻² on 5% PTFE, Cathode 0.25 mg_{Pt} cm⁻² (Alfa Pt/C 40%wt.) on 5% PTFE GDL, dew points 60/60); (C) Polarization curves (scan rate 10 mV s⁻¹) for cells with lowered humidities (Anode and Cathode: 1.25 mg_{Pt} cm⁻² (BASF Pt/C 50%wt.) on 0% PTFE, anode/cathode dew points indicated in the figure legend).

[35–37], and typically occurs when the cell, more specifically the catalyst layers, have difficulty managing water. The instability can often be relieved by lowering the dew points of the feed gases, and cells that may be thought to be low performing can have surprisingly recoverable performances. This is discussed in finer detail below.

Due to the potential for catalyst layer flooding, when the anode and cathode gasses are fed to the cell at full humidification, the amount of water present significantly hinders performance. This flooding limitation at 60/60 is observed in Fig. 2C (and Fig. S2), with polarization data taken for a cell assembled with symmetric Pt/C (50 wt% BASF) electrodes using a 0% PTFE GDL at the anode and cathode. Despite the expected better OH⁻ transport as a result of high AEM hydration, the mass transfer polarization losses impact the cell significantly, preventing the power density of the cell from reaching 200 mW cm⁻². The first approach to reducing excess cell water is to decrease the quantities of water in contact with the MEA through the lowering of the dew points of the incoming gases. As the cathode and anode dew points are gradually lowered, Fig. 2C, flooding is relieved at the electrodes and the achievable power outputs are increased. A minor reduction to the humidifier dew point temperatures to 59/59 is not sufficient to eliminate flooding, and only delays the impact of flooding until the current density reaches approximately 400 mA cm⁻² with observable transport limitations still significantly hindering higher currents and power densities. Further lowering of the gas dew points continued to relieve water issues in the electrodes until an optimum was achieved at 57/55 (calculated relative humidities RH = 87%/79%), where the current density at 0.1 V achieved 2.1 A cm⁻² and the peak power density of the cell was 675 mW cm⁻². However, it is possible to remove too much water and start to dry out the AEM and AEI components, which was the case at 56/56 where a lowering of cell performance was observed.

3.2. Adjusting the gas diffusion electrodes to improve performance

The consumption, generation, and transport of water (illustrated in Fig. 1), along with observation of the mass transfer effects (Fig. 2C), initially suggests that the root cause of performance retardation is anode flooding. Therefore, to improve the water tolerance at the anode, 5% PTFE was incorporated in the GDL, increasing the ability to reject water, which is especially important at higher current densities when water generation and electroosmotic drag are increased. To support the desire of higher cell performance, the anode catalyst was changed from Pt/C to a more

“oxophilic” Pt:Ru/C (2:1) [12,14] with the total amount of Pt loading in the electrode kept constant.

The new anode electrode (0.69 mg_{PtRu} cm⁻² loading, 5% PTFE GDL) was coupled with a Pt/C cathode (Alfa Pt/C 40%wt., 0.35 mg_{Pt} cm⁻² loading, 0% PTFE GDL). As seen in Fig. 3A, the anode water removal was improved even with gas feed dew points of 60/60, leading to double the maximum power density that was achieved using symmetrical Pt/Pt electrodes (Fig. 2C); however, significant water limitations still exist. To ensure that the cathode was supplied with enough water for the ORR, the dew point was maintained at 60 °C while the anode dew point was systematically decreased. With an anode dew point of 59 °C, the mass transport limited current nearly doubles, which results in a significant power density increase. Decreasing the anode water further to a dew point of 58 °C increases the maximum current and power, both to values more than 2.5 times the fully humidified (60/60) condition. Further reducing the anode dew point to 57 °C causes the performance to decrease, suggesting that too much water has been removed.

The highest performance in this system occurred at an anode dew point of 58 °C (calculated RH = 91%) and a cathode dew point of 60 °C (100% RH), with a peak power of 1.05 W cm⁻² at 0.61 V (1.72 A cm⁻²). The high frequency resistance (HFR) at max power was 56 mΩ cm², which is among the best reported in the literature and approaching the order of magnitude for PEMFCs [8,38]. From Fig. 3A, even though reducing the anode RH does alleviate some issues from excess cell water, it is clearly not sufficient to remove all of the mass transport limitations in the cell. Regardless of the anode relative humidity, the cell still demonstrated severe flooding behavior at higher current densities, evident by the immediate decrease in cell voltage in the polarization curves at higher current densities. With 100% RH O₂ fed to the cathode and a GDL containing 0% PTFE, liquid water is likely present in the cathode, where the O₂ may have a harder time diffusing to the triple phase boundary, or need to dissolve in liquid water to react. It follows that water rejection at the cathode (surprisingly) is also important in this system, and the mass transport limited current and voltage fall off may be relieved with improved water management at the cathode.

Therefore, the water rejection properties of the cathode were improved by adding 5% PTFE wetproofing to the cathode GDL. The results of this approach, initially performed exclusively at 100% RH, are shown in Fig. 3B. The presence of PTFE in both gas diffusion layers, combined with the high gas flow rate, resulted in the cell achieving 1.20 W cm⁻² at 0.51 V and 2.28 A cm⁻² with a HFR = 66 mΩ cm², despite full humidity at the anode and cathode; the cell also achieved a maximum current of 3.43 A cm⁻² at 0.15 V.

Fig. 3. Performance data AEMFCs during electrode optimization. Cell Temperature was 60 °C with a 1.0 L min⁻¹ flow rates of H₂ and O₂ at the anode and cathode, respectively. (A) Incorporation of Pt/Ru catalyst and 5% PTFE GDL in anode (anode: 0.69 mg_{PtRu} cm⁻² on 5% PTFE, cathode 0.35 mg_{Pt} cm⁻² (Alfa Pt/C 40%wt.) on 0% PTFE GDL, anode/cathode dew points indicated in the legend; (B) Addition of 5% PTFE to cathode GDL: 60/60 anode/cathode dew points (anode: 0.6 mg_{PtRu} cm⁻² on 5% PTFE, cathode 0.4 mg_{Pt} cm⁻² (Alfa Pt/C 40% wt.) on 5% PTFE GDL), and 54/57 anode cathode dew points (anode: 0.67 mg_{PtRu} cm⁻² on 5% PTFE, cathode 0.53 mg_{Pt} cm⁻² (Alfa Pt/C 40%wt.) on 5% PTFE GDL).

However, even though improved water rejection eliminated the catastrophic water limitations, it can be observed in the forward and backward scan of the 60/60 experiment from Fig. 3B (Fig. S3) that the water problem is not completely solved, and more changes are needed to optimize performance. The return scan achieves a 20% higher maximum power density, expected to be caused by further relief of catalyst layer water when H₂O consumption and transport is increased at higher currents.

Therefore, the dew points for the electrode configuration in Fig. 3B are then optimized to 54/57 °C (calculated RHs = 75%/85%), leading to a power density of 1.4 W cm⁻² at 0.55 V and 2.57 A cm⁻² (HFR = 50 mΩ cm²). This AEMFC is the highest performing reported in the literature to date (Table 1). The lower anode dew point clearly avoided flooding even at current densities nearing 4.0 A cm⁻². Additionally, the lower cathode dew point provided flooding relief without dry-out, supporting the back-diffusion hydration mechanism proposed in this study. IR-correction of the optimized condition results in an IR-free peak power of 1.8 W cm⁻², which shows the potential for peak power gains with tuned ionomer:carbon ratios, catalyst loadings, catalyst layer fabrication and porosity through optimized ink preparation methods, carefully controlled RHs, and the use of thinner AEMs. The concept of increased water mass transport away from the anode with thinner AEMs was recently explored using a pore-filled AEMs and a poly(vinylbenzyl trimethylammonium) ionomer, with some success [25], though the electrodes reported in this prior work flooded significantly even at low current densities (ca. 800 mA/cm²). This again highlights the need for considerable additional experimental and theoretical work in AEMFC electrode engineering.

Overall, the cells that are reported in this work highlight the performances that can be achieved in water balanced AEMFCs, with catalyst layers capable of appropriate water rejection resulting in desirable AEM hydration, strong OH⁻ anion transport, and mitigation of catalyst layer flooding. This performance characteristic, avoiding cathode dry out even at high current density and reduced RH feeds, may be different than observed with AEMFCs containing other materials because of the novelty of the electrode fabrication method used in this work as well as the use of the powder AEI and high ionic conductivity of the ETFE-based AEM used in this study; the water mobility and resulting water back diffusion are, therefore, significantly enhanced [15,17], leading to balanced anode and cathode water with avoidance of anode flooding and cathode dry out. Fig. 4 shows a qualitative comparison of the electrode/membrane water content when back diffusion is able to play a significant

role in the movement and balancing of water (illustrating the key ideas of this work). There is an ideal gas feed humidity where the water at the cathode is maintained and the AEM is properly humidified, despite potentially running the AEMs with gas feeds below 100% RH.

3.3. Influence of H₂ and O₂ gas flow rate

In addition to wetproofing the electrodes, the feed gas flow rate can be used to elucidate water issues in operating fuel cells. By comparing different gas feed flow rates at the anode and cathode using 0% PTFE GDLs, the water removal rate was investigated. Fig. 5A shows the effect of a symmetrical 25% decrease in anode and cathode feed gas flow rates (both decreased from 1.0 L min⁻¹ to 0.75 L min⁻¹). When the flow rate is decreased with cell dew points optimized at 57/55 and the AEMFC being discharged at 0.5 V ($t = 0$), the current rapidly drops from 1250 mA cm⁻² to approximately 500 mA cm⁻². With a 0.5 V discharge hold and 0.75 L min⁻¹, the current response exhibits a highly variable saw tooth pattern, which is typical of catalyst layer flooding.

A comparison of the cell performance at the two flow rates can be observed in Fig. 5B where the higher flow rate relieves the flooding limitation and is able to generate 2.5 × greater power and current densities. The polarization curves were taken after equilibration at each flow rate for 60 min under otherwise identical conditions. The lower flow rate demonstrates a significant mass transfer limitation that initiates very early in the polarization curve (0.8 V and 300 mA cm⁻²). This effect cannot be accounted for by a simple reduction in the reaction rate because of gaseous reactant consumption, as the minimum stoichiometric ratio of feed gases at 1.0 L min⁻¹ are 15 and 30 × reactant consumption for pure H₂ and O₂ respectively.

Further testing with cathode oxygen vs. cathode air (CO₂-free) is shown in Fig. 5C and D, respectively. This data lends support to the idea that higher flow rates lead to improved water removal, as the volumetric flow rates remain the same in both cases, but the cathode supplied with air has only 21% the partial pressure of O₂ in the catalyst layer. The polarization data shows that the volumetric flow rate of the cathode gas is the most important aspect of the need for a high flow rate, as opposed to the specific amount of O₂ provided to the inlet. Lowering the reactant supply by a factor of 5 has minimal effect on performance (reduction in peak power of only 10%), while lowering the volumetric flow rate of the gas feed by a quarter significantly lowers the peak power (by 60%). This

Fig. 4. Schematic showing the hypothesized distribution of water across the AEM and electrodes in an AEMFC, containing a high conductivity AEM with high water back diffusion, with increasing gas stream relative humidity.

Fig. 5. Performance data for a study on varying gas flow rates and oxidant makeup (Anode and Cathode: 1.25 mg_{Pt} cm⁻² (BASF 50%wt.) on a 0% PTFE GDL, with anode/cathode dew points = 57/55 °C). (A) Current response at 0.5 V H₂/O₂ AEMFC discharge with a decrease in gas flow rates from 1.00 to 0.75 L min⁻¹ at $t = 0$; (B) H₂/O₂ AEMFC polarization curves with these two flow rates; (C) H₂/O₂ AEMFC polarization curves with 1.0 L min⁻¹ flow rates with and without IR-correction; (D) Polarization curve with 1.0 L min⁻¹ H₂ and CO₂-free-air.

Fig. 6. Polarization curves for AEMFCs with catalyst layer optimization (Anode: $0.35 \text{ mg}_{\text{PtRu}} \text{ cm}^{-2}$ on 5% PTFE, GDL Cathode $0.25 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ (Alfa 40%wt.) on 5% PTFE GDL): (A) Modifying anode dew point (cell $T = 60^\circ \text{C}$); (B) Modifying cathode dew point (cell $T = 60^\circ \text{C}$); (C) Optimizing both dew points (cell $T = 60^\circ \text{C}$); (D) Cell T and humidity increase. Legend labels = anode dew point/cathode dew point (panel A–C) or anode dew point/cathode dew point/cell (panel D).

demonstrates the impact of water rejection in the electrodes and the importance of this to the overall cell performance.

The cell is further tested with the anode flow rate reduced to 0.2 L min^{-1} to match the molar flow rate of oxygen supplied to the cell under air operation (Fig. S4). Lowering the H_2 flow rate only decreases the performance slightly and does not show the same catastrophic effect seen when lowering the cathode flow rate. When the cathode stream is switched back to O_2 but with a flow rate of only 0.2 L min^{-1} , the cell is unable to hold a current at 0.5 V and “crashed” immediately. These results support the importance of water removal at the cathode.

A working hypothesis for the sudden and severe influence of the flow rate is now discussed. With a flow rate of 1.0 L min^{-1} , the average gas velocity in the single pass serpentine channel is extremely high at 21 mm s^{-1} , and this leads to a pressure drop along the flow path that results in a substantial pressure gradient between passes of the serpentine flow field. This causes the gas to “jump the bar” where a portion of the gas flow preferentially passes through the gas diffusion layer and the catalyst layer, avoiding the accumulation of liquid water. With the lower flow rate, the water can collect in the catalyst layer and GDL, resulting in flooding and preventing adequate O_2 supply to the triple phase boundary. Therefore, other flow designs may increase the “jumping the bar” effect, yielding the positive effect of water removal from the catalyst layers at higher current densities and lower flow rates. This will be the subject of a future study.

3.4. Reducing the catalyst loading

To realize the potential of AEMFCs from a cost perspective, it will

be necessary to lower (and ultimately eliminate) the platinum group metal (PGM) loadings in the catalyst layers. Therefore, the total catalyst loading was reduced by approximately half, with an anode loading of $0.35 \text{ mg}_{\text{PtRu}} \text{ cm}^{-2}$ and a cathode loading of $0.25 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ (Alfa, Pt/C, 40 wt %). Both electrodes were fabricated with 5% PTFE in the GDL. Despite using the three advances discussed - a high flow rate, lower relative humidity, and hydrophobic GDL - the cell experienced water mass transport limitations at all tested dew points (Fig. 6A–C). This is likely due to the thickness of the electrode, where thinner layers lower the water “capacity” of the catalyst layer, or the ability to absorb and transport excess water away from the catalyst during flooding conditions as well as provide water in the case of local dry-out. At full humidity, the cell is unable to sustain a current above 500 mA cm^{-2} , where the only difference from the maximum performing cell in this study (1.4 W cm^{-2} and operation approaching A cm^{-2}) is the thinner catalyst layer. Even under galvanostatic control, the cell crashed and was unable to maintain steady performance at full humidification (Fig. 2B).

One possible way to combat the lower water capacity and inability of the thinner layer to reject water is to increase the cell temperature. The influence of higher operating temperature was investigated using the same cell configuration as Fig. 6A–C, but with an increased cell temperature of 70°C with the setting of both humidifiers to a temperature of 69.5°C (calculated $\text{RH} = 97.9\%$). A comparison between 70°C and the best performing 60°C test with the same cell configuration can be seen in Fig. 6D. Even at 98% RH, the increased temperature mitigates the water issues in the cell that were present at 60°C . This is likely due to the presence of more absolute water content in the vapor phase, along with an increased

ability for the gas flow to accept and discharge water. The increased water management ability shows that higher temperature may be able to alleviate the catalyst layer and GDL flooding while maintaining high levels of hydration for the AEM. This represents a promising avenue for the future application of AEMFCs, although more work must be done in the polymer community to create more chemically and mechanically robust AEMs with high ionic conductivities at temperatures $>60^{\circ}\text{C}$.

4. Conclusions

In this work, it was shown that the amount and balance of water is important in order to achieve high performing anion exchange membrane fuel cells (AEMFC). Cell performance can be systematically increased by tuning the cell water to optimize the dynamic (and sometimes delicate) balance between membrane hydration and electrode flooding/dry-out. It was observed that a number of AEMFC operation conditions can even lead to the flooding of the AEMFC cathode. There are several possible variables that can be controlled to actively manipulate the cell water: gas feed dew points, catalyst layer hydrophobicity, anode and cathode gas flow rates, flow channel design, catalyst layer engineering, and the physicochemical properties of the anion exchange membrane and ionomers. Additionally, operating at higher temperature increases the amount of absolute water in the vapor phase, and likely the water buffering capacity. Future work by our teams will investigate the influence of ionomer:carbon ratio, ionomer ion-exchange capacity and chemistry, electrode fabrication technique, catalyst loading, and catalyst layer porosity on the AEMFC performance.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jpowsour.2017.05.006>.

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