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

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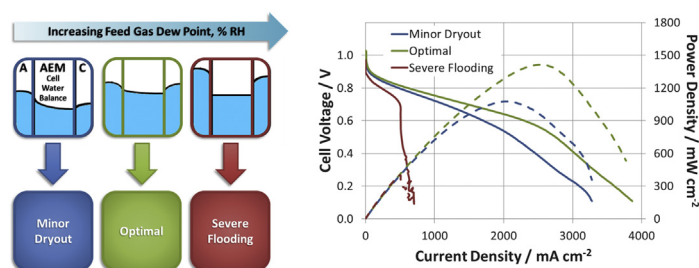
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HIGHLIGHTS

- 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

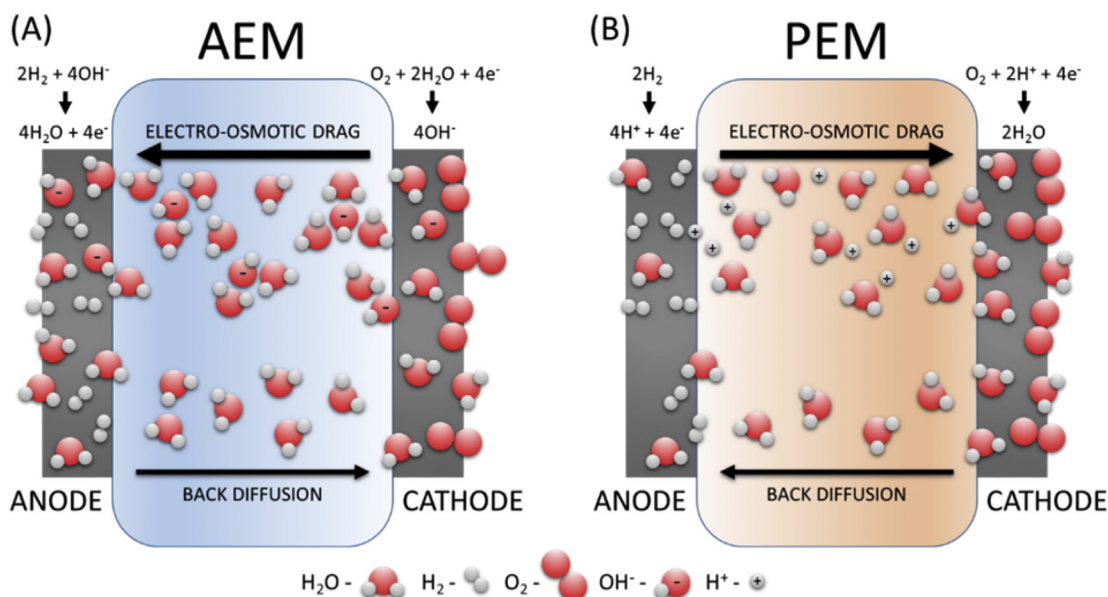


Fig. 1. Schematic comparison of water consumption, generation, migration, and diffusion in AEMFCs (A) and PEMFCs (B).

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