

## ALKALINE FUEL CELLS

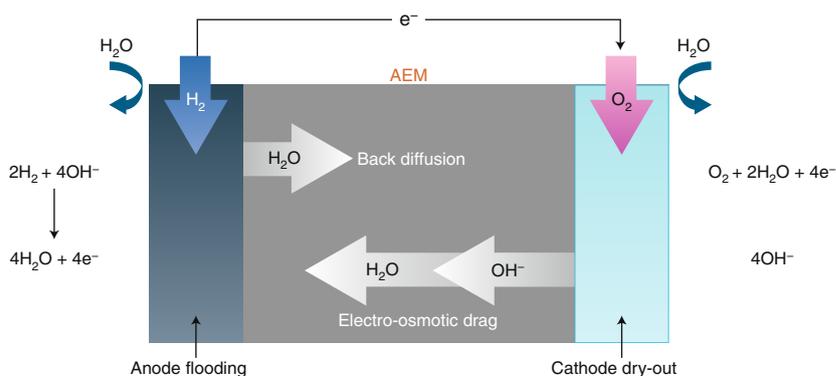
## Water balancing

Water management is an important aspect in the operation of alkaline exchange membrane fuel cells. Now, a lightly cross-linked norbornene polymer membrane is shown to be able to facilitate optimal water transport, leading to exceptionally high power and current density fuel cells.

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Along with batteries, fuel cells also offer a key energy technology for electric vehicles and grid systems. Proton exchange membrane fuel cells (PEMFCs), typically consisting of platinum-based electrodes and water based, acidic polymer membranes, make use of the electrochemical reaction of hydrogen and oxygen to generate electricity at relatively low temperatures. They are one of the incumbent technologies for light duty vehicles. A major drawback of PEMFCs, however, is that their use of precious metal based electrocatalysts leads to high costs. Operating a fuel cell in an alkaline environment, on the other hand, allows for the use of a wide variety of low cost and platinum-free electrocatalysts, as well as inexpensive metal stack hardware<sup>1</sup>. This approach has led to significant interest in developing alkaline-exchange membranes (AEMs) and AEM fuel cells (AEMFCs) in recent years<sup>2</sup>. There has been tremendous progress in improving the hydroxide ion conductivity of AEMs, one of the most important aspects for efficient AEMFC operations. For example, polyhydrocarbon based AEMs can achieve a high hydroxide conductivity of  $\sim 0.1 \text{ S cm}^{-1}$  at  $25^\circ\text{C}$ , approaching that of the proton conductivity for practical PEMFCs<sup>3</sup>. However, water management during cell operation (such as controlling the location and flow of water) has been largely overlooked<sup>4</sup>.

In contrast to PEMFCs, more water is generated at the anode than is consumed at the cathode during AEMFC operation; this intrinsic water imbalance can lead to anode flooding and/or cathode dry-out (Fig. 1), severely limiting the current and power density. Writing in the *Journal of The Electrochemical Society*<sup>5</sup>, Paul A. Kohl and colleagues from the USA report a light cross-linking norbornene-based tetrablock copolymer AEM that is capable of balancing water transport across the cell, leading to an exceptionally high power density of  $3.5 \text{ W cm}^{-2}$  and current density of  $9.7 \text{ A cm}^{-2}$  with pure oxygen at  $0.15 \text{ V}$  and  $80^\circ\text{C}$ .



**Fig. 1 | Water imbalance in an AEMFC operation.** Water is generated at the anode with the  $\text{H}_2$  gas feed and consumed at the cathode with the  $\text{O}_2$  gas feed. For every four electrons transferred, four water molecules are formed at the anode and only two water molecules are reacted at the cathode. This creates a hydration differential between the two electrodes. During the cell operation, water is moved from the cathode to the anode through the AEM by an electro-osmotic drag as  $\text{OH}^-$  is being produced, in addition to a back-diffusion of water from the anode to the cathode. These two processes can lead to imbalanced water transport and thus anode flooding and cathode dry-out.

To avoid electrode flooding/dry-out, it is important for an AEM to have high water permeability. High water permeability can lead to high water of hydration (that is, water molecules are bound into the AEM), which is beneficial for the hydroxide ion conduction. However, excessive water uptake can also occur, which not only leads to excessive unbound free water and potential hazards of flooding in the ion-conducting channels and swelling of the AEM, but also reduces ion conduction and membrane stability. As such, it is important to balance the trade-off between the ionic conductivity and the water uptake.

In their work, Kohl and colleagues choose a norbornene-based tetrablock copolymer, which has a high ion-exchange capacity (IEC,  $3.88 \text{ meq g}^{-1}$ ). IEC describes the total active sites for ion-exchange and often scales with the ion conductivity, but high IEC could also lead to high water uptake in AEMs. To control water uptake at the high IEC membrane, the researchers lightly cross-link the copolymer with *N,N,N,N*-Tetramethyl-1,6-hexanediamine. They find that this is very effective in simultaneously

achieving high ionic conductivity and a small amount of water uptake.

By calculating the number of bound ( $N_{\text{bound}}$ ) and unbound ( $N_{\text{free}}$ ) water molecules per ion group from their differential scanning calorimetry measurements, Kohl and colleagues show that there is a close relationship between  $N_{\text{bound}}/N_{\text{free}}$  and the ionic conductivity. By experimenting with different mole concentration (5 to 20 mol%) of the cross-linker with respect to the available cross-linking sites in the membrane, the researchers are able to find the optimal amount of  $N_{\text{bound}}$  and  $N_{\text{free}}$ , and thus achieve a high conductivity of  $147 \text{ mS cm}^{-1}$ , and modest water uptake of 67%, which eventually leads to the high performance of their AEMFC. Their best power density is obtained in an AEMFC containing a small amount of poly(tetrafluoroethylene) (PTFE, a hydrophobic layer that is often added to the electrodes to help with water transport between them). Therefore, to show that the membrane is having the key effect on facilitating water transport rather than the PTFE, the researchers also demonstrate the

high performance of AEMFCs without the use of PTFE.

As the diffusional flux of water from anode to cathode is inversely proportional to the membrane thickness, Kohl and colleagues also test three AEMs with different membrane thickness. They show that the thinnest AEM (10  $\mu\text{m}$ ) out of the three samples gives the highest power density. They suggest that this is because thinner AEMs induce higher local water gradient, and thus better water back-diffusion. Various dew points of the feed gases are also tested, revealing that the AEMFC performance with thicker membranes having lower water diffusivity is more sensitive to the gas dew points, and thus that the AEMFCs with thicker membranes are more prone to the local dry-out/flooding in the electrodes.

The work of Kohl and colleagues provides an interesting design of AEMs to facilitate water transport and to generate the kind of power density that rivals the best PEMFCs. However, they only report a relatively short-term stability test of 100 h, and when they switch pure oxygen with air, the maximum current drops significantly from 9.5  $\text{A cm}^{-2}$  to 3.5  $\text{A cm}^{-2}$ ; both aspects require further improvements. Furthermore, under more realistic operation conditions such as supplying air at high flow rates (to prevent oxygen transport limitations in the cathode) or in the absence of an external gas humidifier, a local dry-out in the cathode is more likely to occur at elevated temperatures, especially considering that realistic cells are much larger than the 5  $\text{cm}^2$  cell used in Kohl and team's study. Finally, while the effectiveness

of water transport is demonstrated well, a thorough understanding of the mechanistic details of the water dynamics across the fuel cell would be beneficial for future AEM designs. 

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