

Development of Anion Exchange Membranes: A Step towards Non-Noble Metal Fuel Cells

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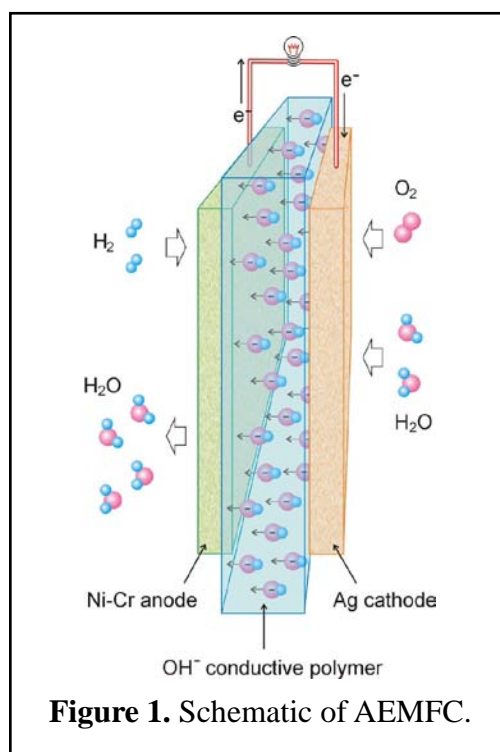
Proton exchange membrane fuel cells (PEMFCs) are regarded as a superior power source due to their quietness, low emissions, and high efficiency.¹ However, the high cost of this system has limited its use to large scale production. The most costly parts in PEMFCs are the perfluorosulfonic acid membrane electrolyte (Nafion[®] membrane) and the scarce and expensive platinum catalyst. Therefore, developing platinum-free fuel cells is necessary for their widespread application.

One alternative is running fuel cells in alkaline environment. Under alkaline conditions, some transition metals and their oxides can serve as stable catalysts for fuel cell reactions.² On the other hand, membrane-based systems prevent carbonate precipitation, mitigate corrosion and simplify the design compared to traditional alkaline fuel cells. The low cost and recent advances of anion exchange membrane fuel cells (AEMFCs) have helped demonstrate the promise that they hold.³ The schematic of AEMFC is shown in **Figure 1**.

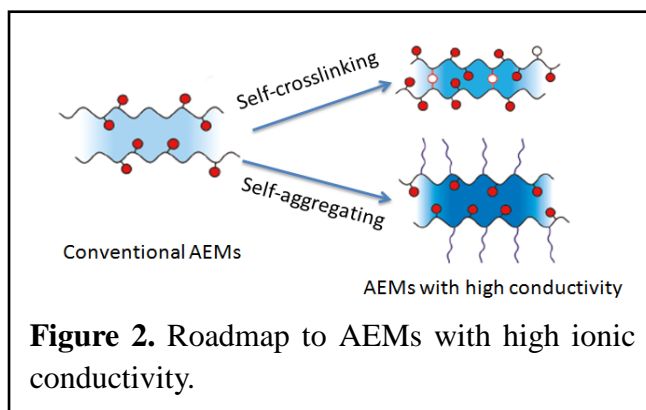
One of the most significant factors that affect the performance of AEMFCs is the quality of the anion exchange membrane (AEM). The development of AEMs has been the center of AEMFCs research. Having a robust synthetic route, high cation stability, high ionic conductivity, good control of membrane morphology and scalability are basic requirements for AEM to be applied in AEMFCs.⁴ These requirements have proved to be challenges for AEM because the conductivity of OH^- is intrinsically lower than H^+ in the aqueous phase and the main functional group in AEM, $-\text{NR}_3^+$, is less stable than $-\text{SO}_3^-$ in Nafion membrane.¹ Specifically, ammonium groups will degrade in alkaline media via Hoffman Elimination, ylide formation or nucleophilic substitution.⁵⁻⁶

To improve the ionic conductivity, researchers have synthesized AEMs with different kinds of headgroups, most commonly ammonium. Yan *et al.* tethered quaternary phosphonium on the backbone.⁷ Their membrane achieved a high ionic conductivity without a high ion-exchange capacity (IEC). Zhang *et al.* succeeded in making a high ionic conductivity AEM using guanidinium as the cation.⁸ Varcoe *et al.* compared the performance of two headgroups: benzyltrimethylammonium (BTM) and benzylmethylimidazolium (BMI).⁹ They found that BMI has higher ionic conductivity while BTM is more stable.

Polymer electrolytes with a high IEC have also been used.^{8,10} However, this is gained at the expense of mechanical strength and increased degree of swelling of the



polymer because high IEC AEMs absorb greater amounts of water. In order to overcome this issue, Zhuang *et al.* reported a self-crosslinking method to reduce polymer swelling.¹¹ By using this method, the polymer can either remain soluble in solution or become cross-linked upon solidification, thus enabling its use as an ionomer. Ionic conductivity can also be improved via hydrophilic and hydrophobic phase separation,¹⁰ which can also be called self-aggregating. Self-aggregating design allows for the aggregation of hydrophilic domains, thus increasing the local ion concentration and improving the effective mobility of OH⁻. In this case, the ionic conductivity of AEM with low IEC can be increased, thus avoiding the drop in the mechanical stability of the polymer.¹ The roadmap to AEMs with high ionic conductivities is shown in **Figure 2**.



In the area of chemical stability, many mechanistic and experimental studies have been reported.^{5-6, 12} Major degradation paths are Hofmann elimination, ylide formation and nucleophilic substitution. Specific conditions such as temperature, degree of hydration, and counter ion form have a significant impact on the chemical stability of various AEMs. Cations with bulky substituted groups have shown relatively high stability;¹³⁻¹⁴ however, the ionic conductivities of those membranes are not comparable to those achieved with high IEC. Tokuyama Corporation has developed several AEMs with both high ionic conductivity and stability.¹⁵⁻¹⁶ The new membrane that they developed shows reasonable durability with slightly less than 5% of the IEC loss after 1,300 hours in 12 wt% EtOH and 20 wt% KOH under 80 °C.

These improvements have been proved encouraging as the first phase for the development of advanced AEMs, yet there are still challenges remaining for AEMs to be commercialized. Key among these are the ionic conductivity, durability of the anion exchange membranes, and the optimization of the membrane electrode assembly preparation.⁴ Therefore, the research priority should be to identify anion-exchange head-groups with acceptable chemical stabilities, excellent conductivities at lower water uptakes.

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