

Anion Exchange Membranes: Current Status and Moving Forward

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ABSTRACT: This short review is meant to provide the reader with highlights in anion exchange membrane research, describe current needs in the field, and point out promising directions for future work. Anion exchange membranes (AEMs) provide one possible route to low platinum or platinum-free fuel cells with the potential for facile oxidation of complex fuels beyond hydrogen and methanol. AEMs and related stable cationic polymers also have applications in energy storage and other electrochemical technologies such as water electrolyzers and redox flow batteries. While anion exchange membranes have been known for a long time in water treatment applications, materials for electrochemical technology with robust mechanical properties in thin film format have only recently become more widely available. High hydroxide and bicarbonate anion conductivity have been demonstrated in a range of AEM formats, but intrinsic stability of the polymers and demonstration of long device lifetime remain major roadblocks.

Novel approaches to stable materials have focused on new types of cations that employ delocalization and steric shielding of the positive center to mitigate nucleophilic attack by hydroxide. A number of promising polymer backbones and membrane architectures have been identified, but limited device testing and a lack of understanding of the degradation mechanisms in operating devices is slowing progress on engineered systems with alkaline fuel cell technology. Our objective is to spur more research in this area to develop fuel cell systems that approach the costs of inexpensive batteries for large-scale applications. © 2013 Wiley Periodicals, Inc. *J. Polym. Sci., Part B: Polym. Phys.* **2013**, *51*, 1727–1735

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Anion exchange membrane fuel cell (AMFC) technology has seen a resurgence with new interest in high pH solid polymer membranes to bring alkaline fuel cells into a membrane format similar to now-common proton exchange membrane fuel cells (PEMFC), Figure 1. Major interest in AMFCs was generated by the early reports of Varcoe and Slade^{1–4} and commercial advances in materials and devices have been pursued by Tokuyama Corporation,⁵ Daihatsu Motor Company,^{6–8} and CellEra, among others. There are now a number of research groups in China, Europe, Japan, Canada, and the United States that are investigating AMFC technology with the objective of providing a new platform for innovation in fuel cells that can break the cost, fuel flexibility, and materials constraints posed by acidic perfluorinated polymers and precious metal catalysts, Figure 2.

The tremendous advances in PEMFC technology over the last couple of decades in the United States, Japan, and Europe have brought fuel cells to the cusp of commercialization in automotive applications. Despite the lack of major consumer market adoption at this time, acid-based fuel cells have seen commer-

cial use in some stationary and mobile applications such as backup or quiet power generators and forklift power plants. The last remaining stumbling blocks for PEMFCs are their use of costly precious metal catalysts and their lack of fuel flexibility. Expensive catalysts in PEMFCs are necessary to facilitate electrochemical reactions at low pH and to resist corrosion during operation. Additionally, hydrogen and methanol have been widely explored as fuels for PEMFC devices and while there are a few other possibilities such as formic acid and dimethyl ether, the number of fuels that can be directly oxidized in a PEMFC without an upstream reformer is limited. These fuels generally have to be very pure to prevent catalyst contamination and cell performance declines during operation. Current PEMFC technology relies on high performance perfluorinated membranes, which have excellent properties and resist peroxide degradation.

With solid polymer electrolyte AMFCs, fluorinated membranes are not necessarily required, although work is underway to evaluate the utility of fluorinated membranes as AEMs, and precious metal catalysts are not needed at least

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at the cathode and they may not be necessary on the anode with more research on hydrogen oxidation under basic conditions.⁹ Moreover, oxidation of carbon-containing fuels,^{10,11} even with impurities, may be easier and carbon-carbon bonds may be oxidized in AMFCs to open up new opportunities in fuel cell deployment. Interest in AMFC technology has spurred work in catalysts^{10,12-14} and device studies are beginning to come online.¹⁵⁻¹⁷ Because commercially available sources of materials specifically optimized for AMFCs are limited, research on anion exchange membranes has become one of the major thrusts of AMFC research and the

development of membrane materials that excel in AMFC applications will be the focus of this review.

The standard method for producing anion exchange membranes in research laboratories has typically involved chloromethylation of an aromatic polymer, such as poly(sulfone) or poly(styrene) and quaternization of the benzylchloride with a tertiary amine to form the quaternary ammonium cationic group tethered to an aromatic ring through a benzyl linkage. These types of materials have been known for a long time¹⁸⁻²¹ and are a facile

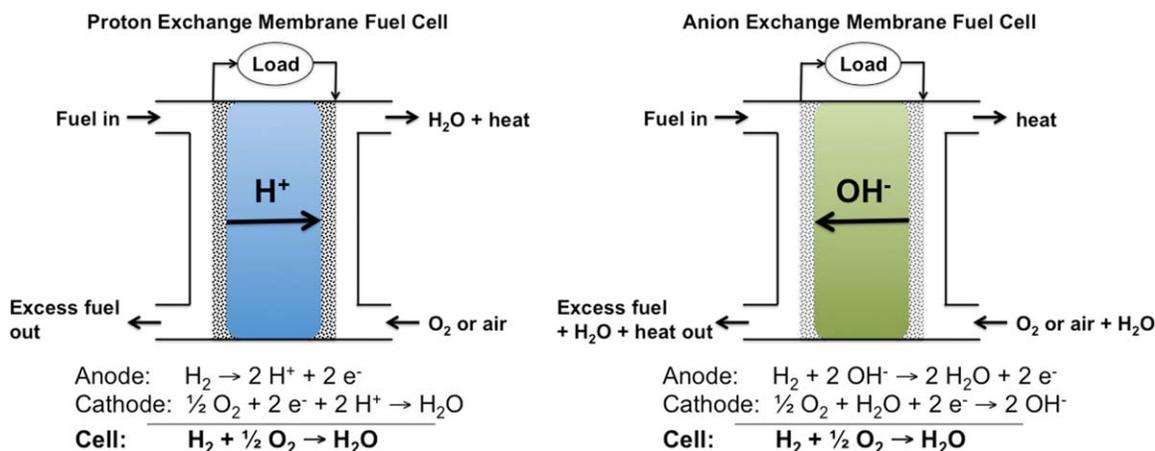


FIGURE 1 (Left) Proton exchange membrane fuel cell schematic and (right) anion exchange membrane fuel cell schematic.

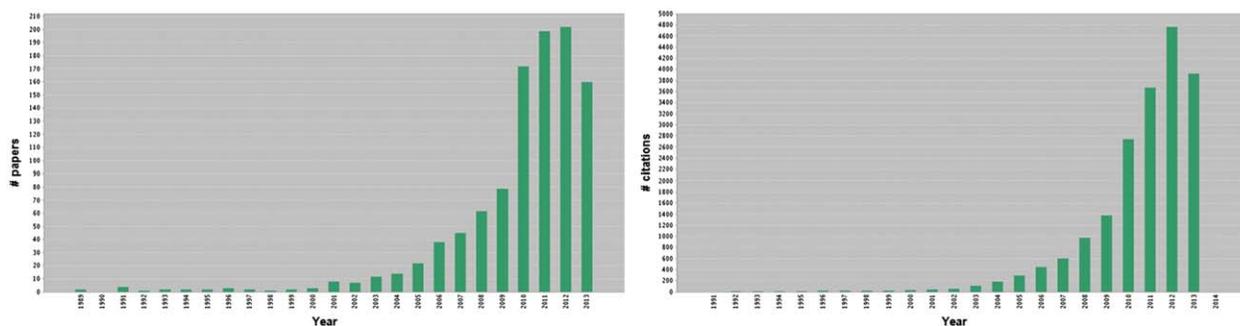


FIGURE 2 Web of science search results for alkaline, alkali, anion, or hydroxyl [hydroxide] exchange membrane and fuel cell; (left) number of papers per year, (right) number of citations per year.

route to anion exchange materials. New routes for synthesizing anion exchange membranes have facilitated systematic studies of these materials beyond chloromethylated aromatic polymers. Specifically, direct polymerization of cationic monomers^{22–26} or precursors to cationic groups²⁷ has expanded the number of approaches to new anion exchange membranes, Figure 3.

Poly(2,6-dimethyl phenylene oxide) (PPO) can be brominated easily to access benzylhalide groups for subsequent quaternization without chloromethylation. This type of process has been explored extensively in the work of Xu, et al.^{28–31} In addition to PPOs, other aromatic polymers with benzylmethyl groups can undergo this reaction as demonstrated by Yan and Hickner³² and Hibbs, et al.³³ PPO is an interesting alternative to poly(sulfone) because in some work on degradation of AEMs the electron-rich PPO backbone has shown significantly higher stability than poly(sulfone).³⁴ Poly(sulfone)s and poly(ketone)s contain strong electron withdrawing groups that decrease the electron density meta to the sulfone or ketone where nucleophilic attack can occur to cause chain scission.³⁵ PPO, poly(phenylene), poly(styrene), and diene-based backbones do not have strong electron withdrawing groups that promote this type of chain scission and may ultimately be more stable platforms for high performance AEMs.

In contrast to PEMFCs where perfluorinated polymers are required to give the membrane stability against attack by peroxide or hydroperoxide radicals,^{36–39} AEMs containing fluorine with hydrogen atoms on the polymer backbone will dehydrofluorinate in the presence of base and fluorine atoms on aromatic rings are not stable at high pH, as well. Many chemists use a base bath, KOH in ethanol contained in a poly(ethylene) bucket, to clean glassware so polymer stability under strongly basic conditions is a challenge. Stability issues arise both in maintaining the integrity of the polymer backbone and also preserving the functionality of the cationic site. A few stabilization techniques for cations have been demonstrated including electronic protection of the positive center^{40,41} and steric shielding of the cation.⁴² However, different stabilization methods may be required for the membrane and for the polymer in the electrode where thin ionomer films may be more susceptible to attack at the electrochemical interface. In addition to benzyl substitution for

the most common benzyl-linked cations from benzylic halides, alkyl substituents on the cationic side chains will readily decompose in the presence of base by Hoffman elimination or in the case of methyl derivatives by methyl substitution. In many cases, a number of decomposition pathways will occur and highly stable cations must guard against all of the common decomposition mechanisms.

Systematic stability studies have been of interest for guiding molecular design of these materials. Tomoi, et al. reported a provocative early study of increased stability using a hexyl or long alkyl or alkyl ether tether between a poly(styrene) backbone and an alkyltrimethyl ammonium cation.⁴³ Hibbs in the current issue of the journal has confirmed this observation with poly(phenylene) backbones and systematically

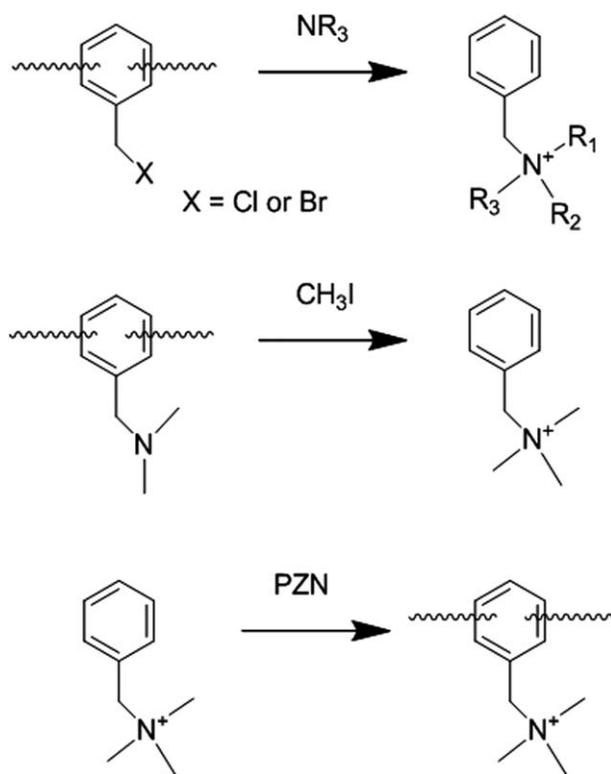


FIGURE 3 Common routes to cationic polymers.

demonstrated materials with excellent stability.⁴⁴ However, these types of cations with long tethers are still difficult to access synthetically. Li, et al. has shown an interesting strategy to improving cation stability by addressing the steric constrains of alkyl ammonium cations with significantly easier synthesis than Tomoi, or Hibbs.^{45,46} Pivovar, et al.⁴⁷⁻⁴⁹ and Varcoe, et al.⁵⁰ have performed systematic work to understand the degradation mechanisms and relative stability of a number of small cations. This informative work has shown that many cation candidates with reasonable stability may exist, but it is difficult to get definitive information on cations that have significantly higher stability than benzyltrimethyl ammonium moieties. Moreover, more reliable methods for assessing stability are needed as there is some inconsistency in the literature data depending on whether degradation is tracked using conductivity or ion exchange capacity measurements, or if the chemical structure changes during degradation are measured directly. The most promising routes to stabilizing ammonium-based and other cations are still being identified, but the community is converging on a multipronged approach to assess stability from different points of view. By generating more consistent degradation data and trying to correlate *ex situ* degradation measurements with *in situ* performance and durability testing, better insight into long-lifetime AEMs in devices will result.

One popular vein of research in anion exchange membranes is the exploration of different cationic functionalities. The perceived poor stability of benzyltrimethyl ammonium cations has been overcome by the construction of larger cations, especially those based on phosphonium, that are stable and may enhance hydroxide conductivity by charge delocalization.^{25,40} The use of these large cations adds additional complexity and cost to the synthesis of the membrane. A number of metal based cations have been proposed including cobalt-cenium⁵¹ and Ru-based complexes.²³ The utility of these is yet to be fully demonstrated and care must be taken to choose cations with redox couples not active in the voltage range of operation of a fuel cell which could lead to the AEM being a mixed electronic and anionic conductor and may have unpredictable effects of the electrode reactions. Other cations that seem to be stable under certain substitution patterns are guanidinium⁵²⁻⁵⁴ and DABCO-based structures.⁵⁵⁻⁵⁷ Substituted imidazolium derivatives provide an important platform for exploring steric shielding of the cation from hydroxide degradation, but in many cases control experiments against benzyltrimethyl ammonium analogs have not been reported, so it has proven difficult to benchmark stability across a number of possible imidazolium structures.⁵⁸⁻⁶⁰

There are some promising demonstrations of device performance but very little lifetime data on AMFCs exists in the open literature. A number of provocative cell lifetime reports have been described in workshops and conferences⁶¹ and academic groups are beginning to make progress in long-lifetime cells.⁶²⁻⁶⁴ One of the challenges in AMFC operation is the mitigation of the effects of CO₂ that enter the cell during air-feed operation. A large cell performance penalty above oxygen concentration effects is observed when the cell is switched from oxygen operation to air operation. It is

thought that the introduction of CO₂ to the cathode causes pH gradients in the cell and may seriously influence the electrochemical activity of the anode and cathode catalysts.^{65,66}

Li, et al. showed that the most stable polymers in *ex situ* stability evaluations in basic solutions did not have a 1:1 correlation with in-device lifetime. This observation points to hydration being critical to achieving long device performance. Since anion exchange membrane fuel cells require water for the cathode reaction and the ionic flux is from cathode to anode, there are important water balance issues that need to be addressed in high-performance devices. Water balance issues have been effectively addressed in PEMFC technology through a large body of work encompassing imaging,⁶⁷⁻⁷⁴ detailed water content and water balance measurements,^{75,76} materials optimization⁷⁷⁻⁷⁹ and modeling,⁸⁰⁻⁸⁴ but very few of these activities have been undertaken for anion exchange membrane fuel cells,⁸⁵ primarily due to limited materials availability and device lifetime. Device operation in the alkaline space is poised to provide a rich area for study, but the materials need more maturation before device engineering can be addressed on many fronts.

A significant challenge in the field is the accurate measurement of AEM hydroxide conductivity. Two issues arise with hydroxide exchanged films: the first being that the hydroxide ions in a membrane will completely react with atmospheric CO₂ within 10 min of exposure to air; and secondly, the cationic groups may not survive the presence of hydroxide and may decompose during exchange to the hydroxide form or measurement at higher temperatures. Films must clearly be checked for decomposition before and after testing if reliable numbers are to be reported. The AEM must be exchanged to the hydroxide form, rigorously washed with degassed distilled water in the absence of CO₂, and the ionic conductivity measured in that state while rigorously excluding CO₂ using high purity blanket gases and degassed water for humidification control. The change in conductivity upon exposure to CO₂ is illustrated in Figure 4 where the conductivity of an AEM is tracked when the water in the conductivity cell was exposed to ambient atmosphere. The ambient atmospheric CO₂ concentration in equilibrium with the water containing the AEM sample was enough to quickly exchange the sample to bicarbonate form. The dilute solution mobility values of hydroxide and bicarbonate provide some rational for the conductivity change. However, the water uptake of an AEM may also be greatly influenced by the counterion form, which can have an effect on conductivity. Thus, rigorous measurements of conductivity, ionic form, and water uptake are needed to untangle the detailed conductivity relationships in AEMs. The problem is that only a very few studies have been done to correlate hydroxide conductivity with other anions. A general rule of thumb can be used to provide ballpark estimates of conductivity in different anion forms. Yan and Hickner³² and Zha, et al.²³ showed that the dilute solution mobility of the mobile species gave predictable correlations between bicarbonate and hydroxide conductivity values.

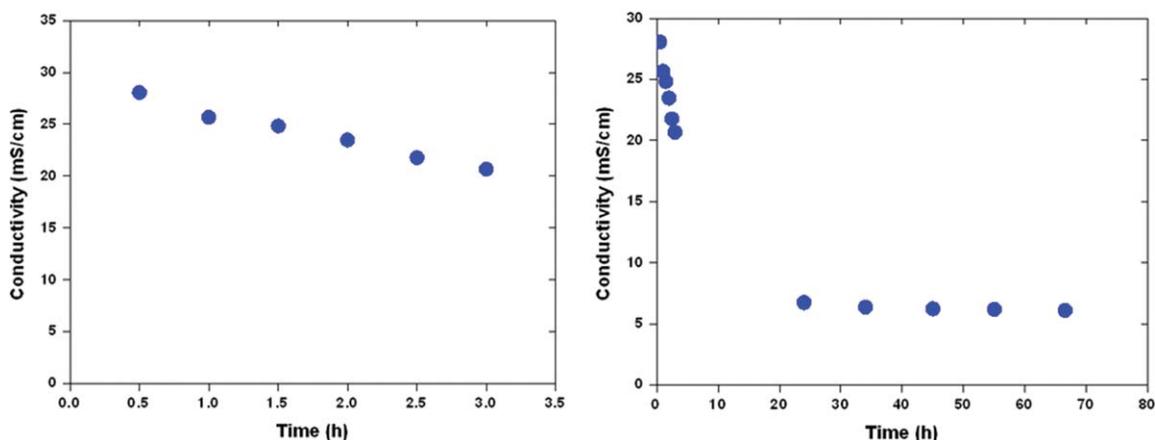


FIGURE 4 Decline in conductivity of a hydroxide form AEM [sample 4:DCDP = 1:5, IEC = 1.4 meq/g, $w_u = 126$ wt %] during conductivity measurements; (left) kept under Ar blanket for up to 3 h, (right) left open to atmosphere after 3 h. Conductivities were measured with samples exposed to liquid water at 30 °C. Data from Ref. 23.

Disabb-Miller, et al. showed that the mobility of the anion in AEMs approached the dilute solution limit at high hydration numbers.⁸⁶

The effects of monovalent cations in anion exchange membranes have been reported by a number of researchers investigating the chloride, bicarbonate, and hydroxide conductivity and water uptake of AEMs. The situation with carbonate and bicarbonate is more complex. An anion exchange membrane in hydroxide form when exposed to air rapidly reacts with the ambient CO₂ to form a mixture of carbonate and bicarbonate in the membrane that then slowly, over the course of about 30 min, reaches an equilibrium that is presumed to be dependent on the pK_a of the system. Because of this fast reaction with CO₂, much of the data reported in the literature for hydroxide conductivity in AEMs is, therefore really for a mixture of carbonate, bicarbonate, and hydroxide conductivity. Obviously, AEMs may be deliberately exchanged with an excess of a carbonate or bicarbonate salt, followed by extensive washing to obtain the pure ionic conductivity of these moieties. Attempts have been made to correlate carbonate conductivity to hydroxide conductivity and a factor of 4.4 has been proposed based on the dilute solution mobility ratio of the anions.³² However, the membranes are not dilute solutions and not enough is known about the mechanisms of ion conduction in these materials, yet, to generalize specific cases.

Many AEMs, especially with IECs above 2.0 meq g⁻¹, do not survive the swelling and deswelling cycles often attempted to obtain ionic conductivity as a function of RH, as these brittle materials either fail during RH changes or become disengaged from the electrodes in the conductivity fixture. In such RH cycling measurements, care must be taken that the measurement reflects the exact ionic state of the membrane, as residual salt may be present. Measurements in liquid water are also potentially suspect as only a small amount of excess base will lead to erroneous results. Initial studies by us when the membrane is washed with degassed deionized

water until the washings are pH neutral suggest that 1×10^{-4} equivalents of Na⁺ remain for each organic cation, which can skew conductivity measurements. Clearly, it is desirable to measure the anionic conductivity of the materials in the carbonate, bicarbonate, or halide form, where these issues do not arise.

Another important point is that the measurement of ionic conductivity for ionic polymers is often reported as an in-plane conductivity from a four-electrode cell using electrochemical impedance spectroscopy to find the low frequency intercept in the Nyquist plot. As the distance between the electrodes is much greater than the film thickness, it may reasonably be assumed that the resistance measured is representative of the ionic resistance in the film. These measurements are valuable screening tools, and activation energies extracted from measurements at constant RH or RH-dependent measurements at constant temperature may be useful in mechanistic evaluations of ionic transport. Generally AEMs that exhibit conductivities greater than 10⁻² S cm⁻¹ under conditions relevant to fuel cell operation should be considered as good candidates for further development if the materials prove to be chemically stable. It should be noted that at very high RH erroneously high ionic conductivities may result from the surface properties of the films.⁸⁷ Through-plane conductivity measurements of membranes are not routinely reported due to errors introduced from electrode-membrane interfacial resistance, however, detailed insight into interfacial resistance issues has been reported by Kim and Pivovar.⁸⁸ While their work was aimed at PEMs in fuel cell devices, the power of their approach to isolate interfacial effects can be used to evaluate the conductivity metrics of AEMs. Therefore, the best approach to examining the conductivity properties of materials in depth is to benchmark in-plane and through-plane measurements with thickness-dependent information. For in-plane measurements, the conductivity should not be influenced by the thickness of the sample, unless there are strong

morphological or surface changes with thickness. For through-plane measurements, multiple measurements of the material as a function of thickness allows unambiguous determination of the material's bulk conductivity as well as quantification of the membrane-electrode interfacial resistance. These thickness-dependent measurements can be performed in dedicated conductivity cells or in cell hardware, assuming the necessary precautions are taken to address CO₂, along with thickness-dependent polarization curve and lifetime performance to gain a comprehensive understanding of how thickness influences membrane and cell performance. While these types of parametric studies are routine for PEMFCs, many first-order studies of AMFC performance have not been performed due to the lack of available materials and limited lifetime of AEM-based devices.

AMFCs have been operated in the expected hydroxide-conducting mode or as low temperature polymeric carbonate fuel cells.^{89,90} To act as a true hydroxide exchange membrane in the fuel cell, carbonate is not produced at the cathode from the 390 ppm of CO₂ present in ambient air which becomes energetically unlikely above 80 °C, and that the fuel is either CO₂-free, is not completely oxidized to CO₂ or that the anode rejects any carbonate or bicarbonate formed on the oxidation of the fuel. AEM fuel cells operated on readily oxidized fuels show lower performance as the CO₂ produced reacts with hydroxide in the anode and dramatically slows anion conductivity and may introduce detrimental pH gradients in the cell. To overcome this limitation, fuels such as methanol are often co-fed with aqueous hydroxide electrolyte, which effectively flushes the carbonate/bicarbonate from the electrode and increases performance by two to three orders of magnitude. In this case where the fuel is co-fed with sodium or potassium hydroxide, the anion exchange membrane acts as more of a cell separator where the hydroxide electrolyte likely plays a large role in the electrode and membrane ion-conducting properties. Very few measurements have been made on AEMs in hydroxide solution to understand how the properties of the polymer influence conductivity. Moreover, the design rules for membranes specifically used in the presence of aqueous base have not been explored and more work is needed if electrolyte-fed systems become a feasible systems approach.

The paradigm of phase separation being important in ion-containing membranes has been firmly established by many studies of ionic domains in PEMs, going back to seminal papers by Hsu and Geirke for perfluorinated membranes⁹¹ and Holdcroft and Mercier for aromatic PEMs.^{92,93} The organic cations of AEMs may have lower segregation strength from the polymer backbone compared to sulfonic acid groups and so AEMs with mechanical integrity and high anionic conductivity are possible in materials that appear to show no obvious phase separation or ionic clustering. Many polymers can be animated and quaternized to an IEC of 2.0 meq g⁻¹ which will give rise to hydroxide conductivities of greater than 50 mS cm⁻¹ without the material displaying excessive swelling. Examining the morphology of these polymers by SAXS allows linking of the microscopic structure with measurements of the overall change in the material's

dimensions.^{94,95} In some instances, no change is observed in the SAXS pattern during hydration, but swelling of the material is observed by microscopy. In other examples, the SAXS intensity increases, but no change in the peak position occurs. Finally, highly ordered samples show swelling in the SAXS patterns with simultaneous visual membrane swelling. Clearly, these types of microscopic morphology and macroscopic swelling behaviors will have an implication on conductivity and other transport properties.

When the ionic domain connectivity is controlled by the polymer topology, for example, when block copolymers have controlled block lengths and volume fractions to promote a specific morphology in the solid state, the morphology-conductivity relationships are usually easier to quantify because of the controlled ordering in the system.^{86,95-99} For most other materials where the base polymer is randomly or statistically functionalized to produce a quaternized polymer, the morphology is often ill-defined and difficult to control or quantify. At this time, it is not known if materials with highly ordered structures, random dispersion of the ions in the membrane or a phase-separated structure is optimal for AEMs or electrode ionomer binders in fuel cell applications. It will eventually be desirable to move anions without excess water in which case ionic conduction by percolation through a highly functionalized polymer may be desirable. Finally, while membrane materials are limited, but becoming more understood, the electrode ionomer is currently a complete mystery concerning its degradation and structure-property performance. The big breakthrough in PEMFC technology to enable commercial viability was thin film electrodes.^{100,101} Ideally, this architecture will continue in AMFCs,¹⁰² but the limited supply of standard materials has hampered efforts to explore the full range of options for membrane electrode assembly construction. Commercially available AEMs are apparently not stable enough in operating AEM fuel cells to facilitate fuel cell optimization without a major program on water balance to preserve the membrane and ionomer properties and delay degradation. Furthermore, it is also becoming apparent that the polymers used as the membrane need to be optimized for use in the cathode and anode catalytic layers. The membrane is designed to be a gas separator, the ionomer in the electrodes should allow rapid diffusion of reactant and products. For example, at the cathode water is a reactant to produce hydroxyl anions and at the anode carbonate must be rejected, which may imply that the polymer in the electrodes have very different chemistry than that of the membrane, whose purpose is only ion conduction and to act as a barrier. Furthermore, methods must be developed for integrating the polymer into the electrode and to minimize any interfacial resistance between the electrode and the membrane. Some reasonable power densities of greater than 300 mW cm⁻² have been reported, but published and validated lifetime data beyond 500 h is rare. It is thought that the stability bottleneck in the first 500–1000 h of device operation in the absence of added base or electrolyte is the stability of the electrode. There is little work investigating the catalyst performance and properties with solid-state polymeric electrolytes or the stability of the electrode-

ionomer interface in AMFCs and the diagnostics for measuring polymer degradation in the membrane and electrode of a working fuel cell need further development.

CONCLUSIONS AND OUTLOOK

Anion exchange membrane properties and device performance and lifetime have progressed significantly in the last 5 years. Innovative materials strategies, detailed structure–property analysis, and insights into materials performance and degradation have pushed the field into the mainstream of fuel cell and energy-related device research. However, there is still a dearth of work in cell performance studies and detailed understanding of anion conductivity and degradation from a polymer structure–property perspective is still being developed. The anion exchange membrane field has progressed rapidly, in part by the significant advancements that have been made in PEMs. There is a wealth of knowledge on the synthesis, processing, and properties of proton-conducting aromatic polymers and some of the lessons learned in PEM research can be rapidly translated to AEMs. Researchers are only beginning to understand anion transport in these complex systems and there is still more work to be done in polymers, especially to address chemical and mechanical stability.

The polymer community has pushed to develop a variety of new materials, new strategies for the synthesis of anion-conducting membranes, and new methods to analyze their performance and degradation characteristics. Perhaps the biggest challenge in anion exchange membranes for electrochemical devices is stability. We now understand the important challenge to achieve large stability improvements and are beginning to build a database of materials candidates for rigorous device testing. However, most currently reported materials have not proven their usefulness in device stability tests lasting more than 1000 h. When this benchmark can routinely be achieved in different device configurations, the detailed work of application-specific cell and stack engineering can proceed apace without the concern of short lifetime cells. To fully exploit the exciting potential of AEM fuel cells, yet more investment and more investigators need to be encouraged to enter the field.

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