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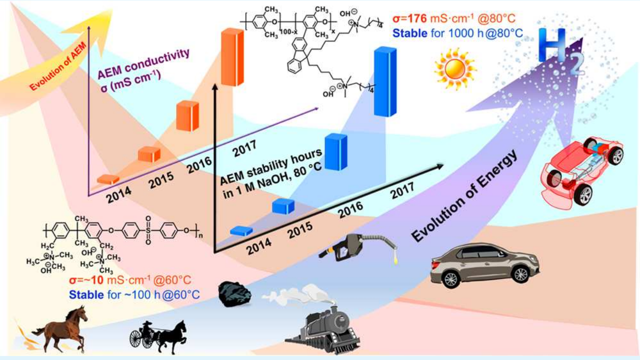
Anion Exchange Membranes' Evolution toward High Hydroxide Ion Conductivity and Alkaline Resiliency

Christopher G. Arges* and Le Zhang

Cain Department of Chemical Engineering, Louisiana State University, Baton Rouge, Louisiana 70803, United States

ABSTRACT: The development of alkaline fuel cells over the past decade has led to exciting developments in low resistant and alkaline stable anion exchange membranes (AEMs). This Review highlights new material chemistries and macromolecular designs that have fueled AEMs with ionic conductivities greater than 100 mS cm^{-1}, while demonstrating stability for extended periods in base bath solutions of 1 M potassium (or sodium) hydroxide solutions at temperature of 80 °C or greater. The new AEMs have led to AEM fuel cells (AEMFCs) with power density values that exceed 1 W cm^{-2} with hydrogen and oxygen. AEM research activities are motivated in large part by their prospect to realize fuel cells free of platinum group metals, which is paramount for cost reduction of fuel cell technology. In addition to highlighting the remarkable achievements of AEMs in the past 4 years, this Review discusses future priorities for the scientific community to address in AEM development. These priorities include stability and conductivity under low humidity or dry conditions, resisting carbonation and oxidation, and AEMFC device stability studies.



KEYWORDS: *alkaline fuel cells, anion exchange membranes, alkaline stability, oxidative stability, carbonation*

1. INTRODUCTION

Alkaline exchange membrane fuel cell (AEMFC) has been an increasing active area of research within the fuel cell community over the past 15 years. Panels a and b of Figure 1 represent the number of works published (Figure 1a) and citations (Figure 1b) for AEMFCs over a 10 year time period (2008 to 2017). The rise in AEMFC research is directly attributed to the enticing prospect of using platinum group metal (PGM) free electrocatalyst for carrying out hydrogen oxidation and oxygen reduction reactions—which is critical to reducing the cost of low temperature fuel cell technology.[1] Switching to alkaline media broadens the material space to design effective non-PGM electrocatalysts for the necessary hydrogen and oxygen redox reactions. Prior to diving into this Review, it is important to retrace the genesis of the non-PGM proposition and it starts with alkaline fuel cells using liquid electrolytes.

Alkaline fuel cells using liquid electrolytes operate effectively with nickel/nickel−metal alloys[2] and silver electrocatalyst[3] for hydrogen oxidation and oxygen reduction.[4] A major drawback of using a liquid electrolyte was their susceptibility to carbonate precipitates—where the carbonate and bicarbonate anions precipitate with sodium and potassium cations. The formation of carbonate species comes from hydroxide anions readily reacting with carbon dioxide (CO_2). Once formed, these precipitates clog up the porous electrodes, causing catastrophic failure of the fuel cell. Replacing the liquid electrolyte with a solid-state hydroxide ion conductor (e.g., an AEM) mitigates the carbonate precipitate problem because the cations are tethered to the polymer backbone.[1] Although early researchers drew inspiration from alkaline fuel cells with liquid electrolytes as motivation for developing AEMFCs, there are some notable differences. Alkaline fuel cells with liquid electrolytes typically tend to operate at higher temperatures, up to 200 °C, under pressure (16−116 psig),[4] while AEMFCs are intended for sub-100 °C operation to prevent dry out of the membrane and maintain membrane ionic conductivity. Although nickel alloys and silver, both non-PGM electrocatalysts, are suitable for liquid electrolyte alkaline fuel cells, they have not displayed the same performance for AEMFCs and today the vast majority of AEMFC reports still rely upon PGM based catalysts (either located in the anode or cathode or both).[5]

In the pursuit of developing AEMFCs, multiple materials challenges were encountered. Some of these problems have been resolved and are highlighted in this Review for AEMFCs. The main hurdles for AEMFCs, currently still obstacles today but not to the same extent reported over a decade ago, are (i) the lack of commercially available AEMs that provide long-term chemical stability over a several-thousand-hour run, minimize carbonate species formation, and yield high current density operation;[6] (ii) anode electrocatalyst for the hydrogen

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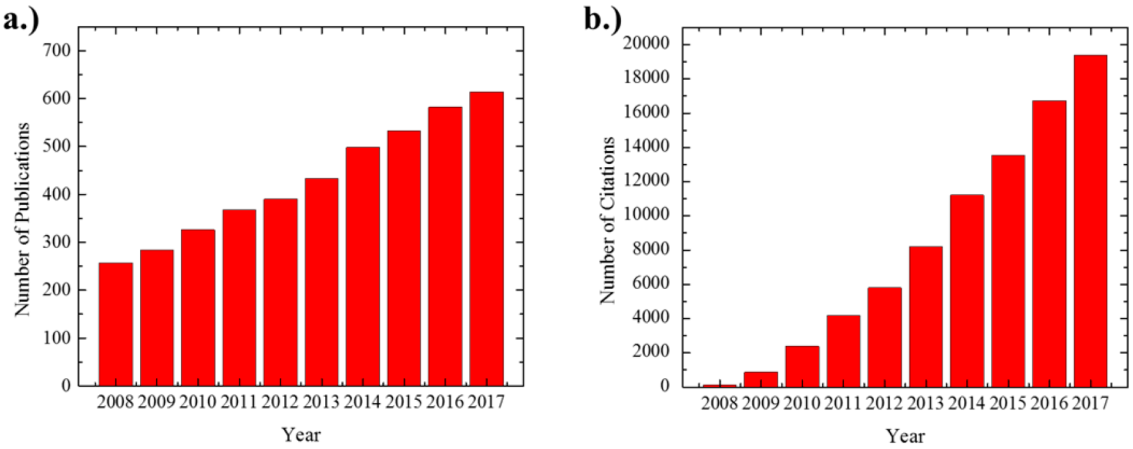

Figure 1. (a) Number of publications for anion exchange membranes geared toward anion exchange membrane fuel cells over the past decade, and (b) number of citations for those works published over that time period (search performed on Mar. 4, 2018). Data generated from Web of Science.

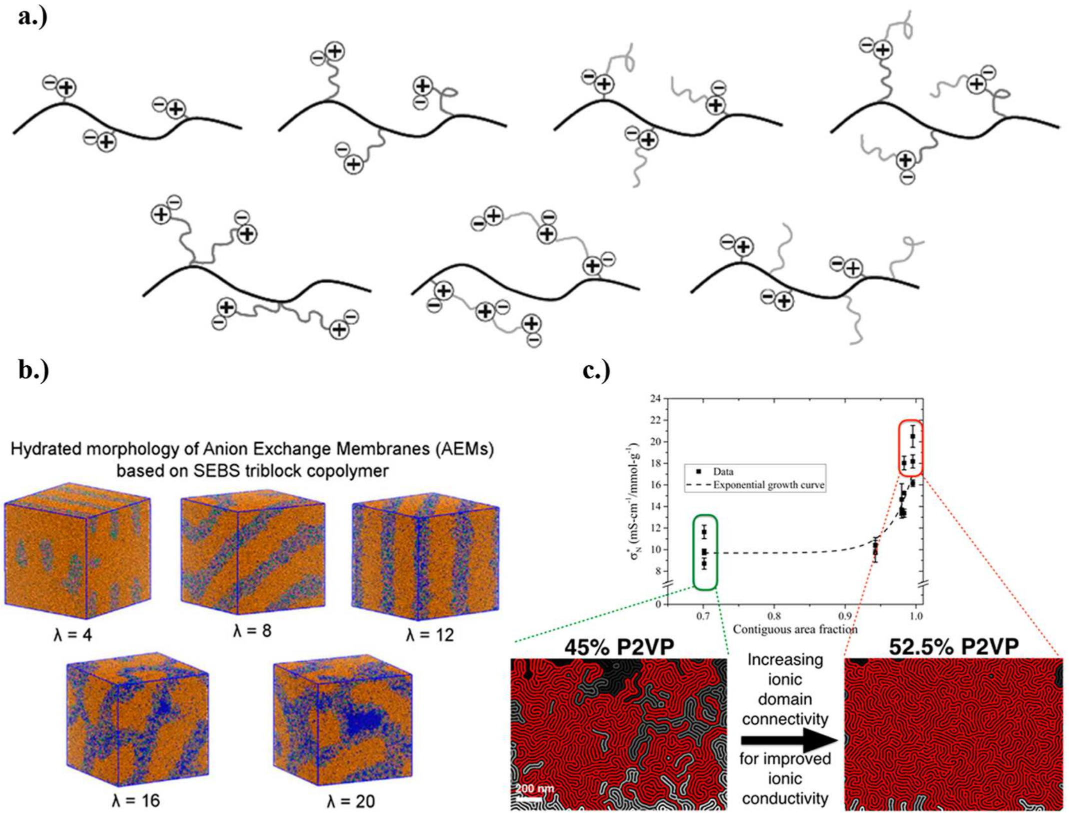

Figure 2. (a) Different tethering strategies (adjacent to polymer backbone, terminal ionic groups with pendant chains, tails to tethered cationic moieties, and multiple cations on a side chain, etc.). Reprinted with permission from ref 16. Copyright 2016 Wiley. (b) Molecular simulation of water uptake in quaternary ammonium based poly(styrene-*block*-ethylene-*random*-butylene-*block*-styrene (SEBS) anion exchange membranes. Reprinted with permission from ref 67. Copyright 2017 American Chemical Society. (c) SEM images of microphase separated thin film anion exchange membrane with different degrees of ionic domain connectivity and its influence on ionic conduction. Reprinted with permission from ref 55. Copyright 2017 Royal Society of Chemistry.

oxidation reaction (HOR) that is comparable to HOR kinetics in proton exchange membrane fuel cells (PEMFCs);[7] and (iii) AEMFC single-cell performance, as determined from polarization data, that is on par with or exceeds their proton exchange membrane fuel cell (PEMFC) counterparts and free of PGMs—this also assumes operation with air and not pure oxygen.[8]

The main objective of this Review is to highlight new and exciting research results of AEMs for AEMFCs. Several notable reviews have covered AEMFCs, for example Varcoe and coworkers,[9,10] Hickner et al.,[11] Gottesfeld et al.,[12], Dekel,[21] and others.[13−20] The late 2017 to early 2018 reviews by Gottesfeld et al.[12] and Dekel[21] differ from this Review, because the former article focuses more on the overall AEMFC system while the latter article centers on cell/system stability; neither of theses articles give a comprehensive assessment on the strides made in AEM functionality and stability within the past 3−4 years—which represents the period of time since the last seminal and comprehensive AEM review by Varcoe and co-workers. At that time, there was no AEM material capable of both hydroxide ion conductivity over 100 mS cm^{-1} and alkaline stability at 80 °C or greater. In this Review, we aim to highlight the new emerging trends in AEM research that are making low resistant and alkaline resilient AEMs possible.

To close the Introduction, it is important to point out that not only has the evolution in AEMs' conductivity and alkaline stability proved transformative for fuel cell technology but these materials are also catalyzing the development of several other important electrochemical technologies and applications that include AEM water electrolysis,[22] redox flow batteries,[23] photoelectrochemical cells,[24] electrochemical reduction of carbon dioxide to added value products,[25] electrochemical reduction of nitrogen to ammonia,[26] lithium−air batteries,[27] carbon dioxide removal,[28] reverse electrodialysis for harnessing salinity gradient power, and electrodialysis[29] and membrane capacitive deionization for water desalination.[30] It is beyond the scope of this Review to discuss AEMs' connection to these technologies and the nuanced differences in AEM properties for these applications versus fuel cells. Overall, the knowledge gained from AEM research for AEMFCs has broadly informed the rationale design of AEMs and has made an indelible impact on other emerging electrochemical technologies.

2. HYDROXIDE ION CONDUCTIVITY AND CARBONATION

2.1. Hydroxide Ion Conductivity. Much AEM research over the past decade centers on improving the ionic conductivity and the alkaline stability of AEMs.[31] Early AEMs used in AEMFCs did not exhibit alkaline stability at elevated temperatures (60 °C or greater) and hydroxide ion conductivity values over 10 mS cm^{-1} were rare.[1] In this section, we focus on strides made in ion conductivity for AEMs. Coates and co-workers in 2010 were the first researchers to produce a hydrocarbon, cross-linked polyethylene AEM with "hydroxide" ionic conductivity over 100 mS cm^{-1} (e.g., 140 mS cm^{-1}, 80 °C).[32] Note: "hydroxide" here represents a mixture of most likely carbonate, bicarbonate, and hydroxide anions due to carbonation of the AEM sample. The carbonation effect will be discussed in greater detail later. However, this AEM suffered from excessive swelling (225%; note: at room temperature) due to the large IEC (2.3 mmol g^{-1}) and selection of backbone chemistry that could not repel excessive water uptake. Zhuang and co-workers in 2012 reported a modified poly(arylene ether sulfone) (PES) AEM that demonstrated over 100 mS cm^{-1} at 80 °C in deionized water with a low IEC and low water uptake (1.0 mmol g^{-1} and 15%; note: at room temperature).[31] This material derived from commercially available PES using tethered side chains with secondary amine linkages that fostered microphase separation. These reports are quite remarkable given that not until too long ago membranes with hydroxide ionic conductivity above 10 mS cm^{-1} were sparse. Today, several AEMs exhibit hydroxide ion conductivity values greater than 100 mS cm^{-1} (tested in the range of 20−90 °C). These low resistant membranes are the byproduct of employing new molecular architectures and chemistries that featured pendant side chains with terminal cation moieties,[33−37] combs,[31,38] cation moieties embedded into the polymer backbone,[39,40] multiple cations on side chains,[41−43] cross-linkers,[44,45] electrospun composite materials with cross-linkers,[46] and block copolymer systems.[47−49] See Figure 2a for a simplified cartoon representation of some of these new molecular architectures. The high ionic conductivity of the newly developed membranes is often attributed to microphase separation at the molecular level, which forms percolated ionic domains for facile hydroxide ion transport across the membrane.[31,38,47−49] Additionally, better distribution of ionic moieties across the membrane, e.g., by optimizing the radiation grafting procedure for poly(ethylene-*random*-tetrafluoroethylene) (ETFE) based AEMs, yields higher ionic conductivity of AEMs.[50,51]

An important AEM property to keep in mind when discussing ionic conductivity is water uptake and dimensional swelling. Early AEM reports with high hydroxide ion conductivity were achieved with very large ion exchange capacity (IEC) values.[52,53] However, these materials suffered from excess water uptake. Excessive water uptake jeopardizes AEM mechanical properties and in some instances can be detrimental to AEM ionic conductivity.[53] Another consequence of excessive water uptake in a fuel cell device is the membrane−electrode delamination that leads to poor contact with the electrode layer. Hence, AEMs with large water uptake values are unsuitable for fuel cell platforms. Elimination of water uptake completely, however, is not an effective strategy for AEMFCs. Condensed water within these membranes forms percolated pathways, such as those seen in Nafion,[54] and this facilitates the dissociation of anions from the tethered cation species. The new membrane architectures mentioned in the previous paragraph not only have facilitated higher ionic conductivity but also have curtailed excess swelling of AEMs by (i) providing a microdomain that is hydrophobic or (ii) utilizing the cation groups more effectively—e.g., uniform distribution across the membrane[51] or a percolated network of aggregated ionic moieties in microphase separated domains across the membrane.[55] It is also important to mention that composite membranes, such as nano-/microparticle AEM mixtures,[56−60] polycations infiltrated into porous or woven supports,[61−64] and electrospun AEMs,[46,65,66] are effective means to improve AEM ionic conductivity while reducing water (or other solvent) uptake values. The particles and the porous support in composite AEMs are nonionic and curb water and/or solvent uptake. The included polycation material in composite AEMs, on the other hand, typically features a high ionic loading for facile ionic conduction. For particle composite AEMs, the particles should be alkaline resistant. Hence, silica or alumina particles should be avoided as they dissolve in base solutions, while zirconia particles are resilient in alkaline media.[56,58,60]

With these new AEM materials emerging, there still is not a clear understanding between microphase separated structures and bulk ionic conductivity. In many cases, the microphase-separated structures characterized via top scanning probe microscopy and electron microscopy convey disjointed ionic domains that lack long-range order and a wide distribution of tortuous pathways.[18] Advanced 3D metrology tools, such as TEM tomography[68]—which is capable of characterizing features from a few nanometers to 50 nm in 3D—and thin film studies (recently performed with Nafion),[69−71] can provide valuable insights that link molecular architecture to ionic conduction.[72] For example, Arges et al. showed that a small population of terminal defects in lamellae forming anion conducting block copolymer electrolytes severely compromised ionic conductivity.[55] The report demonstrated that maximizing the population of percolated ionic domains is paramount for enhancing ionic conduction. One future priority

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for the field is to systematically study different microphase-separated structures, similar to Balsara and co-workers' work with proton exchange membranes,[73−75] to elucidate the role of molecular architecture on anion/hydroxide ion conduction. Additionally, prediction of species transport and water solvation within microphase-separated materials by multiscale molecular simulations, e.g., recent reports by Voth et al.[76] and Paddison and co-workers,[67] will undoubtedly assist in the rational design of new functional AEMs. See Figure 2b for simulated microphase-separated structure of quaternary ammonium poly(styrene-*block*-ethylene-*random*-butylene-*block*-styrene) (QASEBS) AEMs with different water content. SEM images of microphase separated by poly(styrene-*block*-(2-vinylpyridine-*random*-*n*-methylpyridinium) PSbP2VP/NMP$^+$ with varying densities of interconnected pathways and its influence on ionic conductivity are shown in Figure 2c. Finally, noninvasive means of characterization, such as pulsed field gradient NMR and multidimensional NMR correlation spectroscopy,[77,78] are effective means to correlate molecular architectures to multicomponent species transport (e.g., both ions and water). Extending these methods to study species transport under electric fields would be a nice contribution to the field because the methods could identify and quantify the different modes of transport such as shuttling/inverse Grotthuss mechanism, migration, diffusion, and surface site hopping.[13]

It is important to highlight that most literature studies perform AEM hydroxide ion conductivity measurements in liquid deionized water. This is contrary to most PEM studies for fuel cell applications that test proton conductivity under humidified conditions. The scarcity of AEM conductivity studies under humidified conditions is a result of their lower ionic conductivity values when not fully hydrated and the challenge to measure the true hydroxide ion conductivity of AEMs due to the propensity of the hydroxide ion to rapidly convert to carbonate or bicarbonate species in the presence of carbon dioxide (CO_2) in air.[79] Despite the best intentions of researchers to purge CO_2 from the water (e.g., by bubbling nitrogen through the water), most AEMs investigated in the literature are not 100% in the hydroxide ion form. In reality, these AEMs contain a sizable fraction, in some instances 100%,[79] of bicarbonate or carbonate counterions. As stated in the 2014 review by Varcoe and co-workers, the conversion of hydroxide ions to carbonate and bicarbonate species makes it difficult to compare ionic conductivity results of AEMs across the literature.[9] They went on to recommend that AEM studies should also contain ionic conductivity data with other counterions such as chloride or bicarbonate for comparisons. Because of the difficulties of measuring the hydroxide ion conductivity, some use the ionic mobility ratio between hydroxide ions in dilute water solutions versus bicarbonate or chloride ions as a means to predict hydroxide ion conductivity data (e.g., ionic mobility in dilute solutions for different anions: OH^-, 197.6×10^{-5} cm^{-2} V^{-1} s^{-1}; Cl^-, 76.3 cm^{-2} V^{-1} s^{-1}; HCO_3^-, 46.4×10^{-5} cm^{-2} V^{-1} s^{-1}).[80] Measuring conductivity in the bicarbonate, chloride, and bromide form is more reliable because these counterions are stable. However, this simple "ratio" strategy does not take into account other factors that influence ionic conductivity values of AEMs, such as structure-related steric effects, hydration level, and ion pairing. This ratio strategy based on infinitely dilute solution of anion mobility values should be used with caution, and only very limited conclusions can be drawn. Despite the drawback of correlating chloride ion and bicarbonate ion conductivity data to hydroxide ion conductivity, it is recognized that AEM materials with greater chloride or bicarbonate ion conductivities often translate to improved hydroxide ion conductivity.

The best strategy to get relevant hydroxide ion conductivity values is to perform the experiment under controlled environments as reported by Herring and co-workers.[81] They were the first group to develop a glovebox−ionic conductivity system to conduct relevant hydroxide ion conductivity measurements under humidified water vapor in a CO_2 free environment. In their work, they observed that the polyphenylene based AEMs, prepared by Hibbs and Fujimoto,[82] yielded hydroxide ion conductivity values above 85 mS cm^{-1} under humidified conditions. Herring and co-workers have also shown that newly modified poly(ethylene-*random*-tetrafluoroethylene) (ETFE) based AEMs with a more uniform distribution of vinyl benzyl quaternary ammonium groups displayed hydroxide ion conductivity values as high as 159 mS cm^{-1} under humidified conditions in a CO_2 absent environment (see Figure 3 for hydroxide ion conductivity values under 95% relative humidity in a CO_2 free atmosphere).[50] The hydroxide ion conductivity of this type

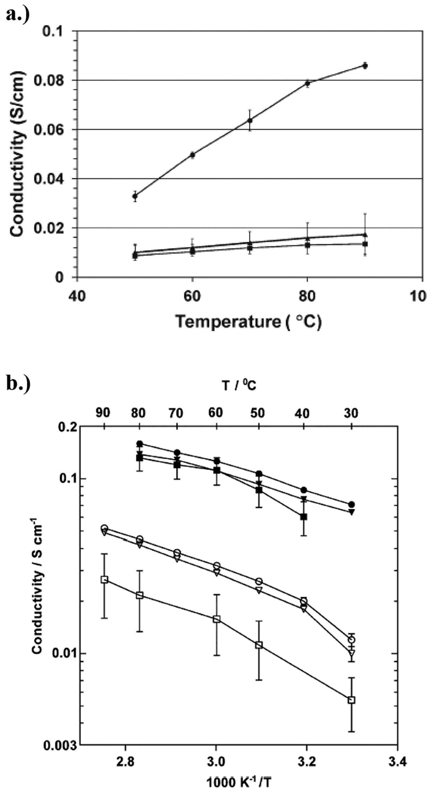

Figure 3. Ionic conductivity of anion exchange membranes under 95% relative humidity environments free of CO_2. (a) Polyphenylene based anion exchange membranes with quaternary benzyl trimethylammonium: circles, hydroxide form; triangles, carbonate form; and squares, bromide form. Reprinted with permission from ref 81. Copyright 2013 Wiley. (b) Poly(ethylene-*random*-tetrafluoroethylene) (ETFE) anion exchange membranes with radiation grafted quaternary benzyl trimethylammonium groups: filled symbols, hydroxide form; open symbols chloride form; squares, quaternary benzyl trimethylammonium cations; circles, quaternary benzyl 1-methylpyrrolidinium cations; inverse triangles, *n*-methylpiperidinium cations. Reprinted from ref 50. Copyright 2016 − Published by the Royal Society of Chemistry.

of AEM was a significant contributor to their impressive AEM fuel cell performance in another study that displayed 1.9 W cm^{-2} with hydrogen and oxygen at 60 °C.[83]

In summary, AEMs with hydroxide ion conductivities at or greater than 100 mS cm^{-1} under humidified conditions are now possible, demonstrating that AEMs can compete with leading PEMs—such as perfluorosulfonic acid materials. However, challenges still persist. AEM conductivity will most likely not be the limiting factor in AEMFC success. AEMs only display adequate hydroxide ion conductivity under fully humidified conditions. Dry conditions, such as at low temperatures or seen during fuel cell start-up, may cause severe ohmic penalties in fuel cell devices, and it is unclear how newly devised leading AEMs behave under drier conditions. Developing AEMs that can conduct hydroxide ions under dry conditions seems warranted for AEMFCs used in vehicle applications—e.g., during vehicle cold start or incidental dry out. Toyota's PEMFC system[84] now operates without an external humidifier because of its thin, reinforced membrane design that facilitates back-diffusion of water from the cathode across the membrane to the anode. Reports by Mustain and co-workers[83,85] and Pivovar[86] illustrate how highly sensitive AEMFC performance is to water content in the electrodes and membranes. Complex water management in these systems may require thin membranes that promote water back-diffusion from the anode to the cathode.[6] One potential strategy to devise AEMs with robust ionic conductivity under varying humidified conditions may also call upon microphase-separated architectures, such as block copolymers, that concentrate the ionic groups and water in one block, while the other hydrophobic block maintains mechanical integrity of the membrane. It is difficult to fully remove the water from ionomers as the water molecules are tightly bound to the fixed cation and counterion groups. Concentrating the ionic groups into percolated, microphase-separated channels may aid facile ion conduction under dry conditions. Another possibility may mimic a design by Guiver and co-workers, where the surface boundary of a PEM contracts and hinders further evaporation and dry out.[87] Extending this concept to AEMs may prove to be a useful strategy. To recap, it is important for the further development of AEMFCs that AEMs conduct under dry conditions.

2.2. AEM Carbonation.

Another significant concern for hydroxide conducting AEMs is maintaining optimal hydroxide ion conductivity and high pH redox kinetics at the respective electrodes in the presence of 400 ppm of CO_2 in terrestrial air. As previously stated, CO_2 readily reacts with hydroxide ions to form unwanted bicarbonate and carbonate anions. These anions lower the pH at the electrodes and compromise redox kinetics as they participate in the redox reaction as opposed to the hydroxide ion. This problem has been originally known since the onset of AEMFC development, but a clear materials strategy has not come to the forefront for dealing with it. Carbonate and bicarbonate species are originally present in the membrane electrode assembly (MEA) when loaded into the fuel cell and can be purged by operating the fuel cell at high current density with hydrogen and oxygen.[88] However, these carbonate species will return when switching the oxidant to terrestrial air.

Researchers at NREL, 3M, and CellEra (acquired by Elbit, Inc.) in 2013 proposed fuel cell operation at temperatures of 80 °C or greater to minimize CO_2 solubility into the AEM material, a principle based upon Henry's Law, to minimize the impact carbonation has on fuel cell performance.[89] Another strategy pursued by CellEra/Elbit Inc. outfitted an AEMFC with a commercially available regenerative CO_2 filter placed in front of the air inlet for alleviating the detriment of CO_2 on fuel cell performance.[12,90] The filter strategy was quite effective, and it reduced CO_2 concentrations from 400 to <5 ppm—a tolerable level, but it is unknown if such a strategy would be acceptable to original equipment manufacturers (OEMs) that may engage in future AEMFC research and development for automotive vehicles. It is worth mentioning that lithium−air battery researchers have also proposed using CO_2 filters to enhance the stability of those batteries that are also being considered for electric vehicles.[27] Besides fuel cells, Parrondo and co-workers reported loss in AEM water electrolyzer performance when exposed to CO_2.[22] Obviating the efficiency loss in water electrolyzer performance necessitated a partitioned environment to prevent any CO_2 inclusion into the system. The steps taken to ameliorate carbonation included bubbling hydrogen and oxygen products into separate KOH baths and keeping the electrolyzer in a glovebox. Because the gap between AEM ion conductivity and AEMFC performance is getting smaller when compared to PEM and PEMFC counterparts,[8] researchers should place a greater priority on resolving the CO_2 carbonation problem. A materials strategy, such as CO_2 phobic materials, could remediate the problem, but the strategy will most likely be difficult to achieve as CO_2 solubility in alkaline media is quite large.[91] Realizing a CO_2 phobic AEM first necessitates investigation of how AEM properties (e.g., chemistry of cation groups, hydration level, and thickness, etc.) influence the extent and rate of carbonation. A recent review[92] by Ziv et al. summarized what is known about AEM carbonation in AEMFCs, but the review added that not much is known about the carbonation phenomena despite its importance to the field. As previously stated, an engineering solution such as a filter on the inlet feed of air or high temperature operation may be the simplest way to proceed albeit at greater system complexity (e.g., regeneration of the filter after it becomes saturated).

3. AEM CHEMICAL STABILITY

3.1. Assessing and Understanding Alkaline Stability.

Arguably the greatest achievement by AEMFC researchers within the past 5 years is the development of alkaline resistant AEM materials that proved practically unattainable for nearly 50 years. Before diving into the materials aspect of AEM alkaline stability, it is important to discuss protocols and methods for assessing AEM alkaline stability. Currently, there is no recognized standard and protocol for assessing AEM alkaline stability—e.g., environment for tests (time, temperature, and concentration of base) and characterization methods (e.g., ion conductivity, IEC, mechanical properties, and spectroscopy). The vast majority of alkaline stability assessments are in the form of immersing AEMs in concentrated potassium hydroxide (KOH) (or sodium hydroxide (NaOH)) solutions (0.5 M up to 20 M) at elevated temperatures (40−140 °C) for a few days (e.g., 48 h) and up to 75 days (3000 h). Because of the progress in alkaline stable AEMs, external alkaline stability assessments are now performed at 80 °C for prolonged periods of time because it represents a more stringent environment over 60 °C and it better reflects the desired operating temperature of AEMFCs. The U.S. Department of Energy Fuel Cell Technologies Office's 2018 Funding

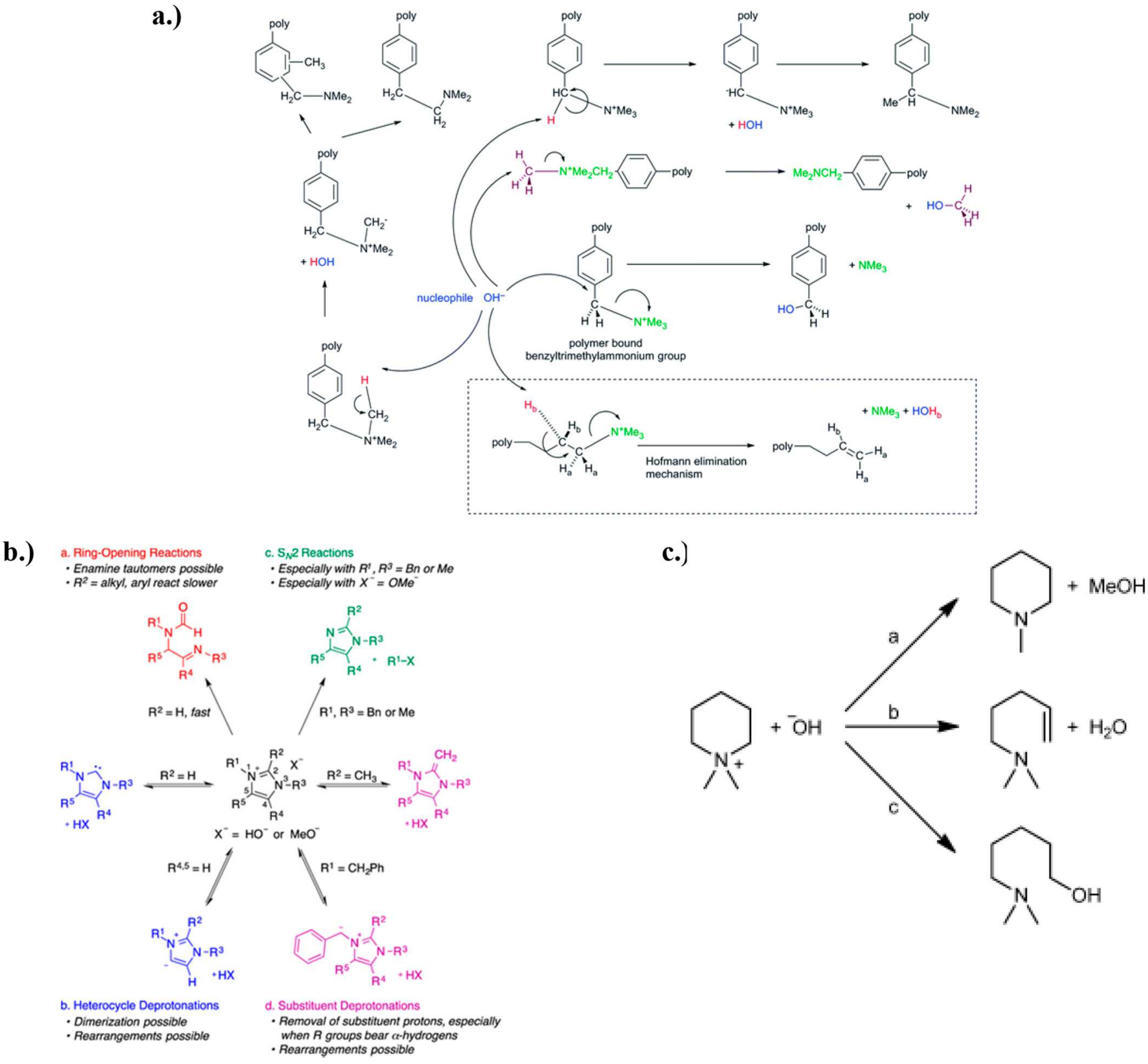

Figure 4. (a) Degradation of quaternary benzyl ammonium groups by hydroxide ions through direct nucleophilic substitution, Hofmann elimination, and rearrangement reactions (via ylide-intermediate degradation pathways). Reprinted from ref 9. Copyright 2014 – Published by the Royal Society of Chemistry. (b) Hydroxide ion initiated degradation of various imidazolium cation model compounds. Reprinted with permission from ref 129. Copyright 2015 American Chemical Society. (c) Degradation of cyclic ammonium cation model compounds by the hydroxide ion: path a, demethylation; path b, ring-opening degradation to form an alkene; path c, ring-opening via direct hydroxylation. Reprinted with permission from ref 132. Copyright 2015 Wiley.

Opportunity Announcement[93] specified AEMFC stability of less than 10% voltage degradation from an initial performance of a current density > 600 mA/cm^2 in H_2/O_2 at 1.5 atm and T > 60 °C over 2000 h with a 50 cm^2 MEA. Because no formal standards exist on the testing methodology for AEM stability, numerous studies relied upon changes in ionic conductivity of the AEM over time in the base bath solution in addition to monitoring changes in IEC under varying temperature and concentrated base conditions. IEC is often characterized by wet-chemistry titration or NMR spectroscopy. A loss in ionic conductivity implied chemical degradation of the tethered cation group. One drawback of assessing stability solely from changes in ionic conductivity relates to the AEM's ability to "age" (i.e., undergo greater water uptake or change in mechanical properties/morphology over time) that would alter its ionic conductivity. Therefore, changes in ionic conductivity may not indicate chemical degradation.

As pointed out in the previous section, it is best practice to measure changes in ionic conductivity not in the hydroxide form because of the aforementioned sensitivity to CO_2. IEC is a practical metric to gauge AEM stability because it directly detects losses in cation head groups[88] (unlike assessing changes in ionic conductivity), but it does not reveal any information about the degradation pathways. Because of carbonation of AEMs, a titration method using acid–base chemistry should be avoided. It is more appropriate to use a specific halide anion (e.g., chloride or bromide) titration such as Mohr[50] or Vohlard[88] titrations. Spectroscopic tools, such as NMR[94] and infrared spectroscopies (coupled with chemometrics),[95] provide useful chemical structure information such as identifying degradation products and quantifying cation concentration. The most prudent approach to characterizing AEM alkaline stability is to not solely rely on one characterization method. Although timely and costly, measuring conductivity, IEC, mechanical properties, in addition to spectroscopic assessments, paint the clearest picture with regard to AEM stability and further enhance the community's understanding of stability limitations.[88]

Although many researchers have utilized base bath soak tests for AEM stability assessments, this accelerated stress test has not been fully validated for mimicking the relevant degradation modes in operating AEMFCs. For example, Hickner and coworkers[96] reported that a base bath stable AEM, made possible by a pendant cation chain design, showed inferior stability during a constant current hold test in a AEMFC device versus an AEM that showed poor base bath stability (an AEM with quaternary benzyl ammonium groups directly adjacent to the polymer backbone). This report emphasizes the importance of connecting AEM failure modes in fuel cell devices to externally performed base bath stability tests (described as ex situ tests). Addressing this knowledge gap will accelerate adoption of more unified testing protocols. As will be shown in this section, there are many reported AEM chemistries with excellent alkaline resistance (less than 25% degradation at temperatures of 80 °C or greater in concentrated base solutions over 7 days)[34−40,45,50,97−109] but only several reports[40,44,88,90,96,97,110−114] that assess AEM stability in operating fuel cells. Device stability studies for AEMs can be difficult as other components (e.g., catalyst, catalyst support, or ionomer) may degrade making it challenging to pinpoint the component that is failing. However, AEMs are now becoming more mature in terms of their alkaline resilience and ionic conductivity, and the field is anticipated to place greater emphasis on device stability studies, which at the end of the day represent the most relevant aspect for AEMFC development.

3.2. Cation Stability. Cation stability for AEMs date as far back as the 1960s—e.g., Trostyanskaya and Makarova observed the degradation of tethered cationic moieties, such as quaternary ammoniums and phosphoniums and ternary sulfoniums, to polymer backbones in the presence of concentrated base solutions.[115] The seminal early review by Varcoe and Slade in 2004 summarized three different degradation routes for cation groups in alkaline media: (i) Hofmann elimination, (ii) nucleophilic substitution to cleave the cation group from the tethered linkage to the polymer backbone (e.g., in most cases debenzylation), and (iii) nucleophilic substitution of dealkylation.[1] Over time, researchers have uncovered ylide-intermediate degradation pathways for degradation,[116−119] which are more prevalent for quaternary phosphonium groups (Wittig reaction)[120,121] and ternary sulfonium[122] groups versus quaternary ammonium groups. The ylide intermediate pathway can be suppressed by modifications of nearby electron donating groups (e.g., methoxy groups substituted onto aryl groups—which was the case for some phosphonium and sulfonium cations used by Yan and co-workers[123−128]). Additionally, degradation mechanisms have been identified and quantified for resonance-stabilized cations such as imidazolium[94,129] and guanidium groups.[130] Panels a−c of Figure 4 report the hydroxide ion perpetrated degradation pathways for mainstream cations used in AEMs. A important work by Bauer and Strathmann[131] in the early 1990s looked at the degradation phenomena of different quaternary ammonium groups, mostly model compounds, to develop an alkaline resistant AEM. That work reported a monoquaternarized DABCO cation tethered to a PES backbone that exhibited stability in 2 M KOH at 40 °C for 150 days (assessed by membrane resistance increase of less than 20%).[131] The selection of the DABCO cation was informed from their model compound studies showing its resiliency to hydroxide ion attack (i.e., quaternary benzyl DABCO—42 min half-life versus a 29 min half-life of quaternary benzyl trimethylammonium in 2 M KOH dissolved in acetonitrile at 160 °C in nitrogen atmosphere). Although DABCO contains β-hydrogen, Bauer and Strathmann stated[131] that it avoided Hofmann elimination because of its caged structure that did not access conformations making Hofmann elimination favorable. Marino and Kreuer[132] have observed that cyclic and noncyclic quaternary ammonium cations in model compound studies display greater alkaline stability over DABCO (cyclic and noncyclic quaternary benzyl ammonium compounds gave half-life values of 4.1−7.2 h versus 1.4 h for quaternary benzyl DABCO in 6 M NaOH at 160 °C; nonbenzyl quaternary cyclic and noncyclic ammonium compounds displayed half-life values of 61.9−110 h versus 13.5 h for quaternary nonbenzyl DABCO cation in 6 M NaOH at 160 °C). One possible explanation for the observed differences is ascribed to the different solvent types used for the alkaline stability studies of the model compounds (Bauer and Strathmann used acetonitrile while Marino and Kreuer used water).

In the early days of AEM research, Hofmann elimination was perceived as a more favorable degradation pathway over direct nucleophilic substitution mechanisms based upon the Bauer and Komkova reports.[131,133] As a result, many researchers pursued cation designs void of β-hydrogens—e.g., quaternary benzyl trimethylammonium groups (most common approach) or quaternary *n*-alkyltrimethylammonium groups with quaternary β-carbons.[134] Although tethered cations free of β-hydrogens were prepared, they could still degrade under direct nucleophilic attack such as debenzylation or dealkylation and rearrangement reactions fostered by ylide intermediates.[9] It will be shown later in the section of tethering strategies for AEMs (section 3.3) that Hofmann elimination is not so prevalent to exclude β-hydrogens in quaternary ammonium cation groups.

An effective strategy for dealing with cation stability problems is to prepare model compounds that can be screened rapidly. The Bauer paper[131] was one of the earliest studies to investigate the alkaline stability of quaternary cation salts, but the model compound studies were performed in concentrated base solutions with glycol[132] or acetonitrile[131] solvent as opposed to water. Changing the solvent from water to another one, such as glycol or a mixture of water and another solvent, adjusts the dielectric constant of the medium opening up new degradation pathways and different rates of cation degradation[135] that may not be relevant for AEMFCs. Mixed solvents featuring water or solvents with no water are selected because they can dissolve the linear AEM polymer and model compounds. In recent years, additional model compound studies, some prominent ones by Coates and co-workers,[129] Pivovar and co-workers,[117] Mohanty and Bae,[135] Hickner and

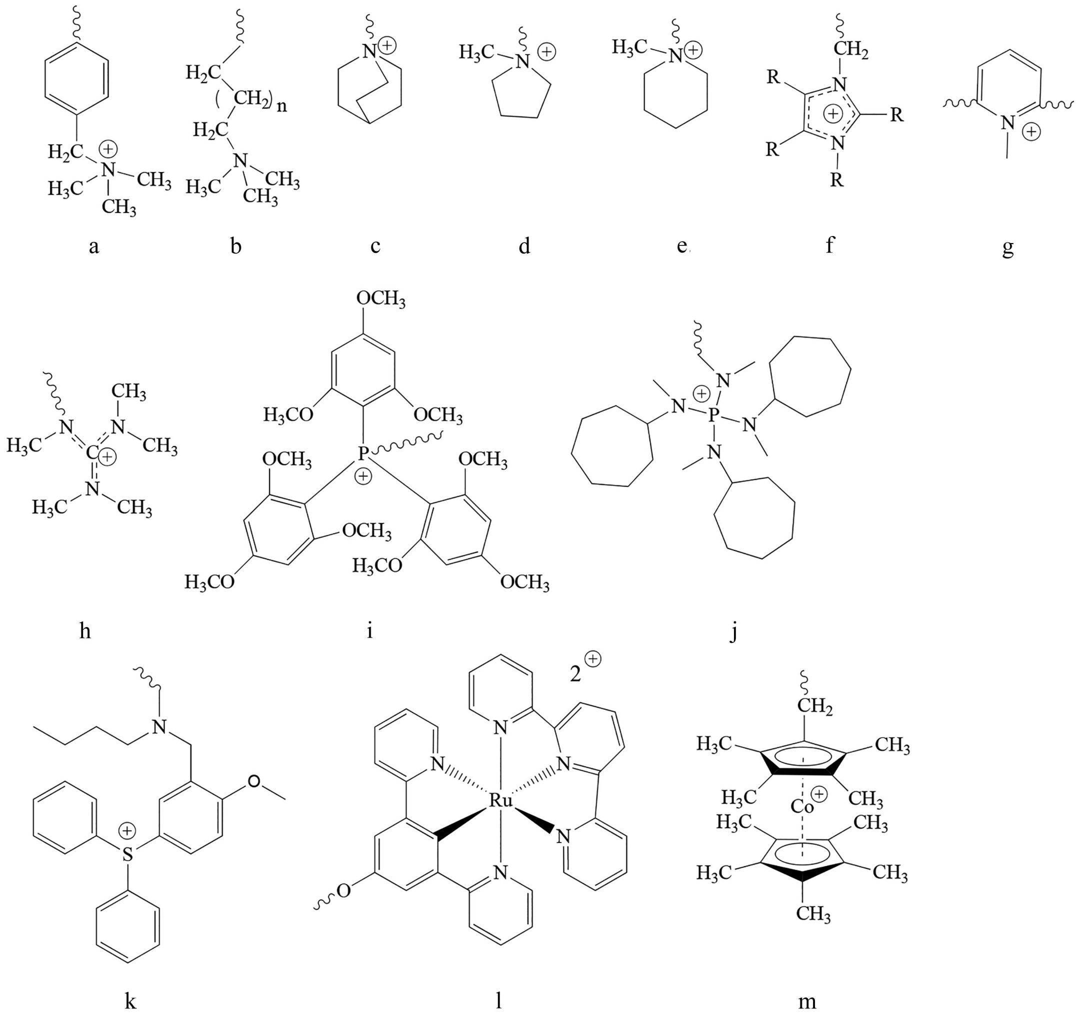

Figure 5. Several types of tethered cation chemistries used in AEMs. (a) Quaternary benzyl ammonium. Reprinted from ref 9. Copyright 2014 – Published by the Royal Society of Chemistry. (b) *n*-Alkyl-trimethylammonium. Adapted with permission from ref 38. Copyright 2017 American Chemical Society. (c) Quinuclidium. Reprinted with permission from ref 88. Copyright 2013, The Electrochemical Society. (d) *n*-Methylpyrrolidinium. Reprinted from ref 50. Copyright 2016 – Published by the Royal Society of Chemistry. (e) *n*-Methylpiperidinium. Reprinted from ref 50. Copyright 2016 – Published by the Royal Society of Chemistry. (f) 1,2-Dimethylimidazolium. Adpated with permission from ref 129. Copyright 2015 American Chemical Society. (g) Pyridinium. Adapted with permission from ref 151. Copyright 2014 Royal Society of Chemistry. (h) Pentamethyl guanidium. Adapted with permission from ref 130. Copyright 2013 American Chemical Society. (i) Tris(2,4,6-trimethoxyphenyl)phosphonium. Adapted with permission from ref 123. Copyright 2009 Wiley. (j) Tetrakis(dialkylamino)phosphonium. Adapated with permission from ref 146. Copyright 2012 American Chemical Society. (k) Methoxy-substituted triarylsulfonium. Adapted with permission from ref 127. Copyright 2012 Royal Society of Chemistry. (l) Bis(terpyridine)ruthenium(II). Adapted with permission from ref 80. Copyright 2012 American Chemical Society. (m) Permethyl cobaltocenium. Reprinted from ref 149, Creative Commons Attribution 4.0 International License (https://creativecommons.org/licenses/by/4.0/legalcode). Copyright 2015 – Published by the Nature Publishing Group.

co-workers,[136,137] and Marino and Kreuer,[132] have used more appropriate solvent systems and have expanded the types of cation moieties that can potentially be used in AEMs. This Review cannot possibly summarize all of the key findings in these model compound studies in detail as they contain a wealth of knowledge. Instead, we refer readers to those excellent papers. Some key takeaways from these studies highlight that (i) quaternary ammonium groups with long alkyl substituent(s) away from aryl or electron withdrawing substituents can be resilient for extended periods of time in alkaline media at elevated temperatures (above 80 °C),[135] and (ii) completely substituted imidazolium groups[110,129,138,139] with electron donating substituents show substantial improvement in alkaline stability over conventional imidazolium groups, such as 1-methylimidazolium or 1,2-dimethylimidazolium groups. Hence, reducing electron withdrawing groups, and adding electron donating groups, improves quaternary ammonium and imidazolium groups' alkaline stability. More electron rich moieties that are in close vicinity to the cation groups lower the hydroxide ions' propensity for attack. Nonprotected C2 sites in imidazolium cations degrade through a ring-opening mechanism[94,129,140] (see Figure 4b). Replacing the acidic protons in imidazolium rings with electron donating carbon moieties minimizes ring-opening degradation mechanisms and enhances alkaline stability of the cation group. Additionally, poly(benzimidazolium) based AEMs[99,101,141−143] that contain sterically hindered and substituted imidazolium cation moieties incorporated along the polymer backbone, by Holdcroft and co-workers, have shown remarkable stability (10 M KOH at 100 °C up to 7 days). Steric hindrance can make it difficult for the hydroxide ion to access and attack the cation. Discussion on quaternary ammonium cations with long *n*-alkyl

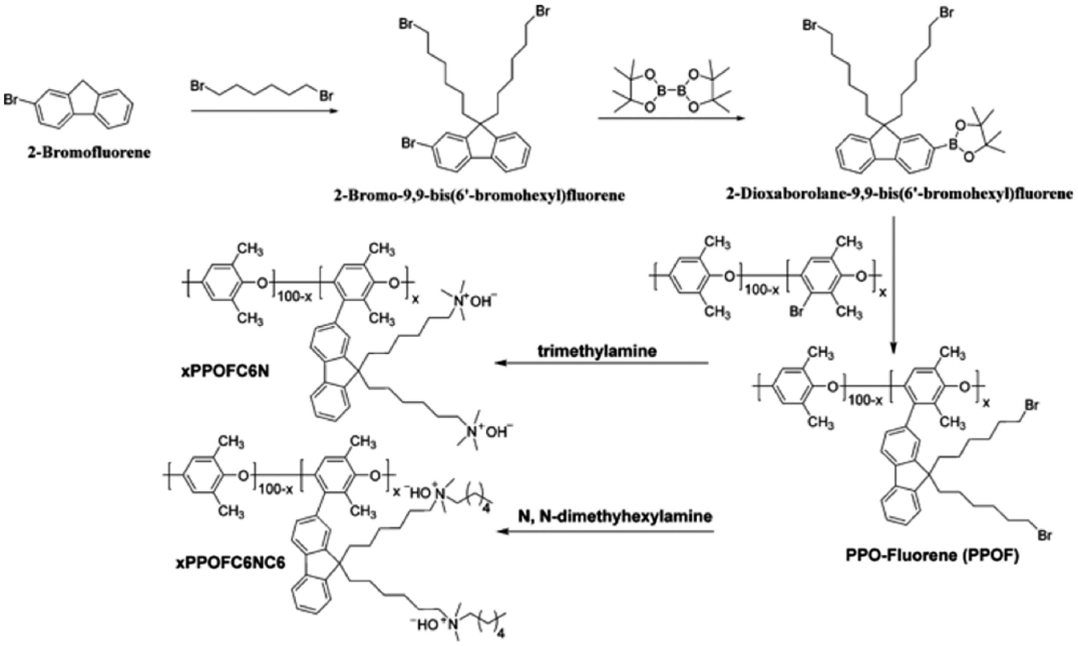

Figure 6. Synthesis scheme to prepare an alkaline stable anion exchange membrane—poly(2,6-dimethyl-1,4-phenylene oxide) with a fluorene tether that contains *n*-alkyl ammonium cation groups. This AEM was stable in 1 M NaOH for 40 days or greater at 80 °C. Reprinted with permission from ref 34. Copyright 2016 American Chemical Society.

tethering groups to the polymer backbone will be covered in section 3.3 as it relates to cation tethering strategies to polymer backbones.

One of the emerging trends observed in the AEM literature is the enhanced alkaline stability of cyclic, monoquaternarized ammonium groups. Five-ring and six-ring cyclic ammonium groups have shown exceptional stability in both model compound studies[132] and AEM studies[39,40,45,105,144] because of these cations' ring strain. Plus, the free base conjugates of these groups are low cost and commercially available, making their incorporation into AEMs straightforward. However, these cyclic ammonium groups still degrade under nucleophilic substitution by a ring-opening mechanism that leaves behind alkenes (see Figure 4c).[50,132] Another subset of cationic moieties with outstanding alkaline resistance is the *n*-alkylaminophosphonium groups (aka as phosphazenium groups) originally devised by Schwesinger and co-workers.[145] Noonan et al. adopted these resonance-stabilized cationic groups for AEMs in poly(ethylene) backbones resulting in alkaline resistance in 1 M KOH at 80 °C for 22 days.[146] The *n*-alkylaminophosophonium groups display excellent base stability due to the charge delocalization along several moieties. Guanidium based cations have been less effective in displaying alkaline stability.[100,147] Unlike alkylaminophosophonium groups, the guanidium-type cations contain carbocations that are highly susceptible to nucleophilic attack by the hydroxide ion. The final class of cations to survey is the ones based upon metal cation centers, such as ruthenium, cobalt, and nickel, in bis(terpyridine) structure[80,148] and permethyl cobaltocenium.[149,150] These classes of cations need to be designed with a redox potential range that will not undergo oxidation or reduction when operated in an AEMFC. The recent reports of cationic groups featuring metal centers with organic moieties for AEMs offer promising stability at 80 °C in concentrated base solutions for extended periods of time. But, these materials are still in their infancy and merit further investigation. Figure 5 summarizes a wide-ranging and fairly representative list of cation group chemistries used in AEMs.

3.3. Tethering of Cations to Polymer Backbones for Enhancing Alkaline Stability. An equally important factor in selecting an alkaline stable cation moiety is the tethering linkage to the polymer backbone. Tomoi and co-workers were one of the earliest groups to examine the role of alkyl spacer length on quaternary ammonium groups' stability for polystyrene based anion exchange resins.[152] Their work demonstrated that an *n*-alkyl chain with more than three carbon centers enhanced the alkaline stability of the cationic group. Each -CH_2- is electron donating, and often a *n*-alkyl chain greater than three carbons improves alkaline stability. Komkova et al. observed a similar effect with bis-quaternary ammonium cross-linkers with different *n*-alkyl chain lengths between the two cations.[133] In general, bis-quaternary ammonium cations (i.e., two positively charged cation groups) in close proximity to each other are more susceptible to degradation.[131] Because the quaternarized nitrogen center is electron deficient, it is essentially an electron withdrawing group and thus two quaternarized nitrogen centers (bis-quaternary ammonium groups) create a local environment that is too electron withdrawing leading to cation degradation in high pH solutions. The tethering linkage of the cation to the polymer backbone garnered more attention after a series of works published in 2012 to 2013[88,153,154] that revealed benzyl ammonium groups adjacent to poly(arylene ether) backbones triggered degradation of chemical bonds in the backbone despite the pristine polymer being stable under the same conditions. Hibbs, an early adopter of a spacer strategy, showed that *n*-hexyl alkyl chains with terminal quaternary trimethylammonium cations attached to polyphenylene based AEMs enhanced cation stability (e.g., quaternary trimethylammonium with *n*-hexyl spacer displayed close to 100% retention of IEC under 4 M KOH at 90 °C for 14 days—an extremely stringent alkaline stability test).[100] Because of these

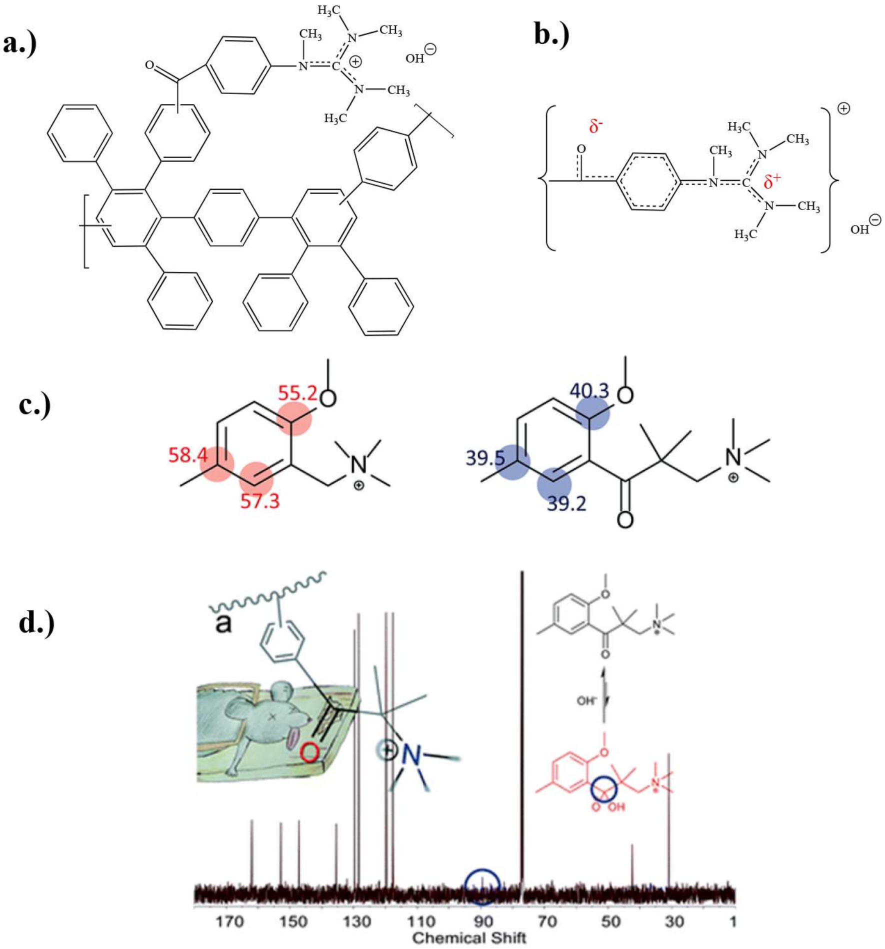

Figure 7. (a) Polyphenylene with tethered acetyl-phenyl-pentamethyl guanidium cation anion exchange membrane (PGP AEM). Reprinted from ref 113. U.S. Department of Energy, 2017. (b) Conceptual schematic of the extended resonance structure at the tethering linkage between the cation and polymer backbone. Reprinted from ref 113. U.S. Department of Energy, 2017. (c) Calculated electrostatic potentials of quaternary ammonium compounds with and without the acetyl linkage for extended resonance. The acetyl moiety lowered the electrostatic potentials values for nucleophilic attack by the hydroxide ion. Reprinted with permission from ref 157. Copyright 2017 Royal Society of Chemistry. (d) Exchange of the hydroxide ion with the acetyl linkage in model quaternary ammonium compounds. Reprinted with permission from ref 157. Copyright 2017 Royal Society of Chemistry.

early studies, significant strides by numerous researchers have devised stable AEMs with tethering strategies and backbone chemistries featuring quaternary ammonium groups. A general trend emerging is that *n*-alkyl spacers, often greater than four carbon units, with terminal cation groups or multiple cation groups on a side chain yield alkaline stable AEMs[34−38,96,98,100,103−109] at temperatures of 80 °C or greater in concentrated base solutions (1 M KOH or NaOH or greater)—but there are some outliers to this trend.[155,156] *n*-Alkyl spacers aid cation stability because the alkyl groups are electron donating. More electron donating groups in close proximity to the cation diminish the hydroxide ion's ability to engage in nucleophilic attack. Figure 6 shows one synthetic route to attain AEMs with *n*-alkyl tethered quaternary ammonium groups, and this AEM has demonstrated excellent alkaline stability (1 M NaOH at 80 °C for over 40 days).[34] The profound impact of the *n*-alkyl tethering strategy demonstrates that Hofmann elimination on *β*-carbons in quaternary ammonium groups with *n*-alkyl chains is not so favorable to exclude their use, and exotic cation chemistry is not required for alkaline stable AEMs because widely accessible quaternary ammonium groups can be used. Furthermore, the results highlight that the tethering strategy is of great importance for both cation and backbone stability in AEMs.

Finally, an interesting and recent concept to realize alkaline stable AEMs is the strategy of resonance over a multitude of chemical units. Kim recently reported a polyphenylene AEM with a ketone tether that links the guanidium cation to the polymer backbone resulting in exceptional alkaline stability at 0.5 M KOH at 80 °C for a thousand hours.[113] This linkage strategy extends the delocalized electron deficiency of the cation over several moieties, decreasing the affinity for hydroxide ion nucleophilic attack. This observation was also seen recently for an AEM that used a ketone moiety to tether quaternary trimethylammonium groups to the PES backbone.[157] Panels a and b of Figure 7 convey the extended resonance structures in AEMs. Figure 7c shows how the resonance structures reduce the electrostatic potential for hydroxide ion nucleophilic attack (from density functional theory calculations), and Figure 7d depicts how other moieties in the resonance structure react with the hydroxide ion.[157]

3.4. Selection of Appropriate Polymer Backbones with Alkaline Stability.

The discussion for AEM stability to this point has solely focused on cation and tethering strategies.

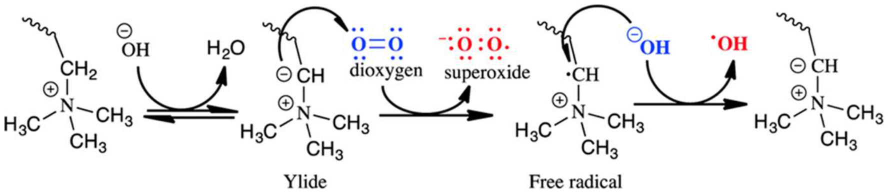

Figure 8. Formation of superoxide and hydroxyl radicals fostered by ylide intermediates in quaternary ammonium cation groups and oxygen. These reactive oxygen species (ROS) can cause degradation of both the quaternary ammonium group and polymer backbone. Reprinted with permission from ref 160. Copyright 2016 Royal Society of Chemistry.

The key priority in designing an alkaline resilient AEM starts with selecting an alkaline stable base polymer. The term "base polymer" corresponds to the backbone polymer chemistry free of the cationic moieties. For example, the base polymer poly(vinyldiene fluoride) (PVDF) is unsuitable for alkaline applications as it degrades rapidly via dehydrofluorination[158] in base solutions. ETFE is an alkaline stable polymer backbone, and base resistant AEMs have been realized with this material.[50] Alkaline stable AEMs, 1 M KOH at 80 °C for extended periods of time, have been prepared from poly(2,6-dimethyl 1,4-phenylene oxide) (PPO) polymers.[34,38,42] But, this pristine polymer can degrade under extreme alkaline conditions (40% NaOH at 80 °C for 300 h),[159] and thus promising new PPO based AEM chemistries may have long-term stability concerns. An early class of poly(arylene ether) based AEMs were derived from chloromethylating PES (either Radel or Udel variants) and were popular to use for initial fuel cell studies because of their ease of preparation. However, PES based AEMs featuring quaternary ammonium cations at the benzyl position weakened the bonds in the polymer backbone (e.g., the ether bond) making these moieties susceptible to hydrolysis by hydroxide ion attack despite the pristine polymer being extremely resilient in alkaline media.[128,129] It is worth mentioning that backbone degradation was also observed for PPO AEMs with cation groups placed at the benzyl position.[88,96,153,154] Arges et al.[88,153] postulated that the electron withdrawing cation groups in close proximity at the benzyl position spurred the weakening of the chemical bonds in the polymer backbone triggering the hydrolysis reactions. The backbone degradation may also be due to the formation of reactive oxygen species (ROS) catalyzed by the presence of oxygen and benzylic quaternary ammonium groups in an alkaline environment (this mechanism will be discussed further in section 3.5).[132,160] From these results, it is clear that researchers cannot ignore polymer−cation interactions and should not draw definitive conclusions about the prospects for AEM stability from polymer or model compound studies alone.

3.5. Question, Is Oxidative Stability a Concern for AEMs Used in AEMFCs?

One key reason polymer backbones composed mainly of arylene moieties, such as PPO and PES, are selected relates to their excellent oxidative stability. But, only a few reports within the past few years make the case for oxidative stability for AEMFCs. Ether free poly(arylene) backbone chemistries for AEMs, such as the poly(phenylene) backbones synthesized by Hibbs and the materials prepared by Bae and co-workers, should provide robust oxidative stability, and they have already displayed exceptional alkaline stability.[100,103,107,161] However, none of these pristine polymer backbone chemistries are commercially available, making widespread adoption and assessment by the research community difficult. Poly(aliphatic) based AEMs based on styrene copolymers offer better benzyl cation alkaline stability when compared to PPO and PES—as indicated by studies of Hickner and co-workers[136,137] and Bae and co-workers.[97,161] The better stability of benzyl cations on poly(aliphatic) backbones versus poly(arylene ether) backbones is ascribed to the less electron withdrawing moieties (i.e., less aryl groups) in the poly(aliphatic) backbones. Polystyrene polymers and their triblock variants (e.g., the commercially available poly(styrene-*block*-ethylene-*random*-butylene-*block*-styrene (SEBS); manufactured by the Kraton Corp.) are good candidates for producing alkaline stable AEMs because of their commercial availability and ease to functionalize with cation groups. Several reports already document the preparation of AEMs from SEBS polymers.[97,162−165] However, poly(aliphatic) backbones easily decompose under strong oxidizing environments[166] as the carbon−carbon single bonds in the backbone are quite labile.

Right now, there are several literature reports focused on oxidative degradation of AEMs for AEMFCs.[6,167] Marino and Kreuer discussed that benzylic cations can foster formation of radical species and carbocations that enable other possible degradation pathways of AEMs in fuel cell environments.[132] Ramani and co-workers recently observed superoxide radical formation in operating AEMFC devices[168] using an in situ fluorescence technique and a fluorescent molecular probe sensitive to superoxide radicals. They also reported that benzyl quaternary ammonium groups catalyze the formation of reactive oxygen species in concentrated base solutions[160] saturated with oxygen (see Figure 8). The ROS generation, observed through a ^{31}P NMP spin trap technique, was enhanced in oxygen saturated KOH solutions leading to rapid degradation of the cationic moieties in AEMs, and it could be responsible for PPO and PES backbone degradation because of its strong oxidizing power (rather than hydrolysis by the hydroxide ion). Switching the cationic group to a quaternary phosphonium moiety mitigated the formation of ROS. The detection of ROS, catalyzed by quaternary ammonium head groups is quite important and would potentially explain the recent observations by Hickner and Li and co-workers that a superior alkaline stable AEM failed faster than a nonalkaline resistant AEM in an AEMFC device—i.e., oxidative stability may also be a significant concern in AEMFCs. Finally, it should be pointed out that Fenton's test for assessing AEM alkaline stability in alkaline environments is not particularly useful. The Fenton's test only favors hydroxyl and hydroperoxyl radicals under acidic conditions,[169,170] but these radicals are not formed under alkaline conditions (unlike the superoxide radical).

If oxidative stability is a concern for AEMFCs, researchers should devise materials that display both oxidative and alkaline stability. This may represent a monumental task, but new advancements in perfluorinated or partially fluorinated back-

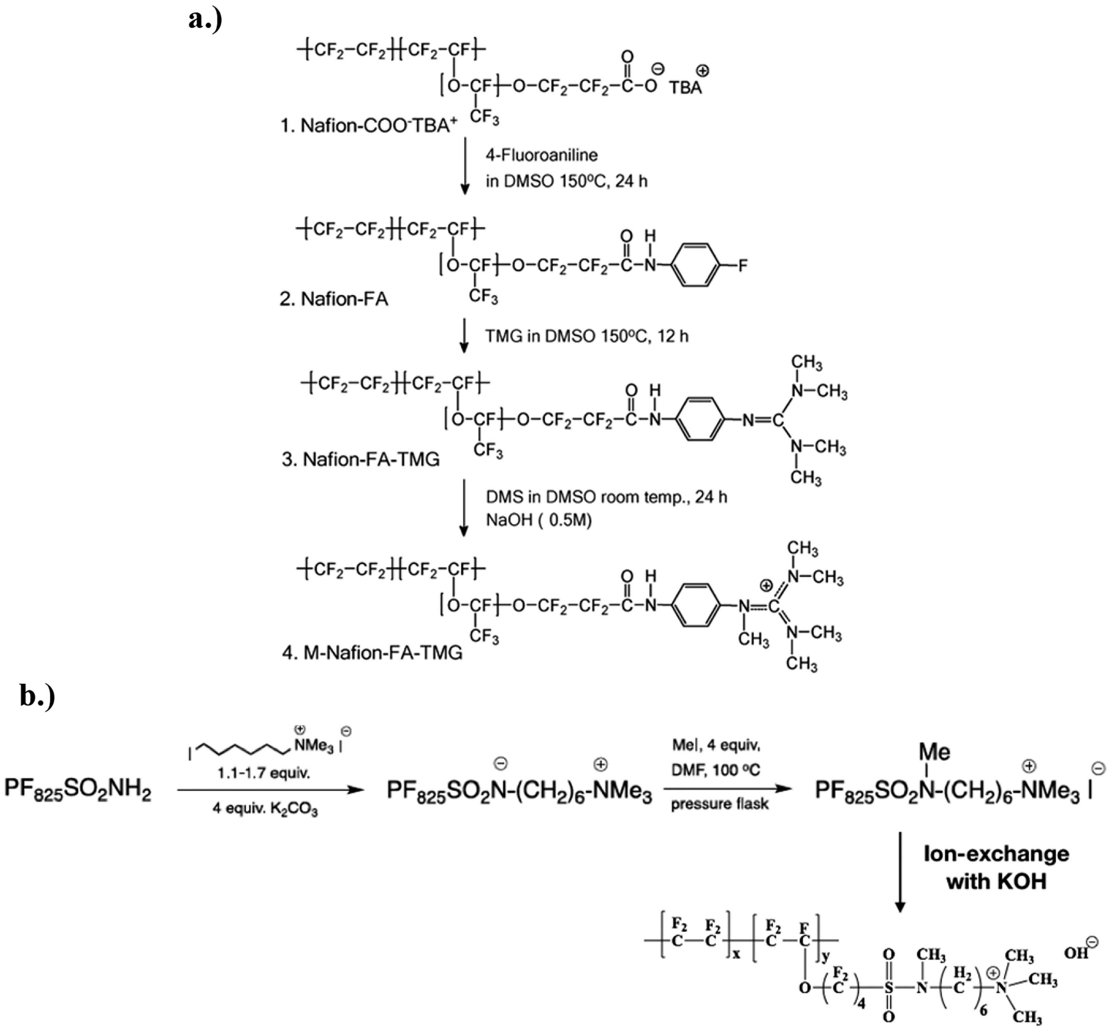

Figure 9. Preparation of perfluorinated anion exchange membranes from a.) the carboxylate form of Nafion. Reprinted with permission from ref 130. Copyright 2013 American Chemical Society. (b) Sulfonyl fluoride form of 3M's perfluorosulfonic acid polymer precursor (note: Generation 2 variant). Adapted with permission of Electrochemical Society, from ref 175, copyright 2017; permission conveyed through Copyright Clearance Center, Inc.

bone based AEMs may provide a solution to this conundrum. The radiation grafted ETFE based AEMs have shown good alkaline stability (less than 20% degradation after exposure to 1 M KOH at 80 C for 28 days) but have not been assessed in terms of oxidative stability.[50] Perfluorinated backbone chemistries, which are used in today's PEMFC technology, have some of the best oxidative stability available, but making them into alkaline resistant AEMs has proved to be difficult. It was originally thought that the electron withdrawing character of the fluorine rich polymer backbone would spur nucleophilic attack by the hydroxide ion on the quaternary ammonium group.[171] Tos-flex, sold by the Tosoh Corp., is a perfluorinated based AEM,[172] but it is no longer available. Kim and co-workers[130] and Pivovar and co-workers[173−175,178] have produced alkaline stable AEMs from the carboxylate and sulfonyl fluoride precursors of perfluorinated proton exchange membrane precursors using tethering strategies[86] (see Figure 9 for generalized synthesis procedure). These new perfluorinated membranes have shown alkaline stability in 1 M KOH at 80 °C for hundreds of hours; however, the weak link in these materials is not the degradation of the cation but the tethering linkages to the polymer backbone. Improving the alkaline stability of the cation linkage is important for further development of perfluorinated AEMs. It is important to highlight that preparation of these AEMs hails from commercially available precursors of proton exchange membranes. Hence, perfluorinated AEMs derived from proton exchange membrane precursors may accelerate AEM availability on the commercial market as the synthesis methods are mature and the starting materials are already produced in large quantities.

3.6. Hydration Level and Its Role in the Alkaline Stability of AEMs. Another stability aspect that merits further priority is the alkaline resistance under dry conditions. As previously stated, most stability studies are performed under fully hydrated, concentrated base solutions. AEMFCs, on the other hand, operate under humidified conditions. Density functional theory (DFT) simulations predict that the hydroxide ion's affinity for nucleophilic attack is more favorable under drier conditions.[116,118] They inferred this effect by changing the dielectric constant during DFT simulations (see Figure 10a). Model compound studies[176,177] have also shown that changing the dielectric constant of the solvent medium, away from water, also accelerates degradation.

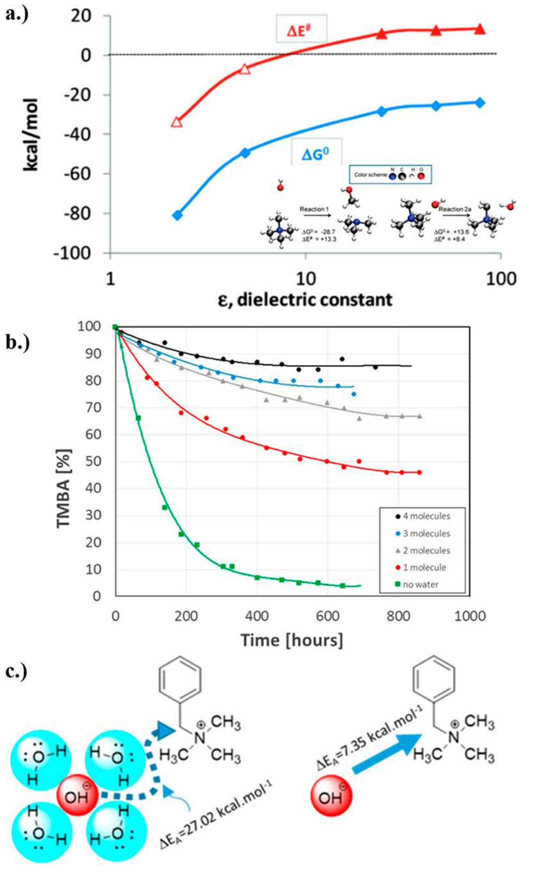

Figure 10. (a) Density functional theory simulation of the activation energy barrier and Gibbs free energy change of the activated intermediate for hydroxide ion nucleophilic attack on a quaternary tetramethylammonium group as a function of dielectric constant. Reprinted with permission from ref 116. Copyright 2008 American Chemical Society. (b) Degradation rate of quaternary benzyl trimethylammonium hydroxide as a function of water content. Reprinted with permission from ref 176. Copyright 2017 American Chemical Society.

Dekel and co-workers[176] observed a commensurability trend between model quaternary ammonium cation compound stability and amount of water present in the solvent system (see Figure 10b). They also extended this technique to a multitude of cation model compounds.[177] However, assessing the level of hydration on AEM and model compound stability by changing the composition of a liquid solvent may not mimic the degradation rate and mechanisms in AEMFCs. For example, mixed alcohol−water solvent systems (as a means to alter the dielectric constant) with metal hydroxide salt may form alkoxide (e.g., methoxide or ethoxide) species that can oxidize the AEM or model compound materials. To understand the challenge of finding a base stable compound material, it is important to recognize that base baths, water−alcohol mixtures with metal hydroxide salts, are used to clean glassware with polymer residues. Because of the dynamic operation of an AEMFC with respect to water content in the cell, AEM stability in the hydroxide form under various levels of humidification is a priority. After AEMFC device stability studies, postmortem analysis can be used to check for the existence of backbone, cation, or tethering linkage degradation. Herring and co-workers used their controlled glovebox setup to demonstrate the stability of ETFE-QA AEM under 95% RH in the hydroxide form at 60 °C for over 300 h. This technique should be adopted for higher temperatures, such as 80 or 90 °C, and under various levels of humidification. Another possibility to assess AEM alkaline stability under dry conditions is by testing the AEMs, prepared into MEAs, in an AEMFC test stand. The challenge with this approach is decoupling AEM degradation to other material component degradation (e.g., binder, catalyst, and/or catalyst support) and isolating whether it is hydroxide ion induced degradation or degradation caused by ROS.

3.7. AEM Stability Studies in AEMFC Devices.

As previously mentioned earlier, less than 15 reports[37,40,44,88,90,96,97,110−113] on AEMFC cell stability exist. Most studies operate the cell under constant current and monitor changes in voltage or hold constant voltage and monitor changes in current. In both approaches, the area specific resistance is also monitored, and sometimes electrochemical impedance spectra are recorded before and after the test to identify origins of component failure. These tests provide an assessment of AEMFC stability.

Arges et al. examined the changes in the impedance spectra before and after a constant current hold test and observed increases in the high frequency resistance (HFR) as well as charge-transfer resistance (R_{CT}).[88] The HFR corresponded to AEM degradation, and it was postulated that the increase in R_{CT} was attributed to ionomer degradation in the electrode layer, and not catalyst or catalyst support degradation, because the test was performed over 12 h—a short period of time. Wang and co-workers[165] employed SEBS based AEM as separator with different AEM binders and tested the in situ stability of the fuel cell. HFR was monitored for 12 h with constant voltage (0.55 V) hold. They stated that the increase of resistance was due to the deteriorated interface between the membrane and electrode. Kim and co-workers[97] observed greater polarization of an AEMFC MEA after holding the cell at 0.3 V for 110 h at 60 or 80 °C. Although the power density was compromised in their QASEBS AEM MEA after the constant voltage hold test, the HFR decreased and was not responsible for the loss in MEA performance. The authors assigned the decrease of the HFR to conditioning of the AEM and the drop in performance due to degradation in the electrode layer. Pivovar[178] demonstrated that an AEMFC demonstrates greater longevity when using an ETFE ionomer (nearly 200 h in the AEMFC at 60 °C) with a perfluorinated AEM separator as opposed to a perfluorinated AEI with a perfluorinated AEM separator. The implication of the results from Kim and co-workers[97] and Pivovar[178] highlight that alkaline resistant AEMs are stable in AEMFC devices, but other reasons, such as ionomer and/or catalyst/catalyst support or electrode−membrane delamination, are the source of AEMFC instability. Zhuang and co-workers[40] assessed AEMFC stability using a quaternary ammonium poly(*n*-methylpiperidine-*co*-*p*-terphenyl) AEM with hydrogen and clean air at 80 °C a constant current density of 200 mA cm^{-2}. This AEMFC showed minor degradation, 57 mV loss, over 125 h (note: the voltage decay rate accelerated after 125 h). It should be noted this test was performed with clean air and not with pure oxygen (the bulk majority of other evaluations in the literature). Because oxidative degradation represents a concern for AEMFCs, one would anticipate better stability with clean air as the oxidant over pure oxygen. Figure 11 shows AEMFC stability results from Kim and co-workers,[97] Pivovar,[178] and Zhuang and co-workers.[40] Hickner and co-

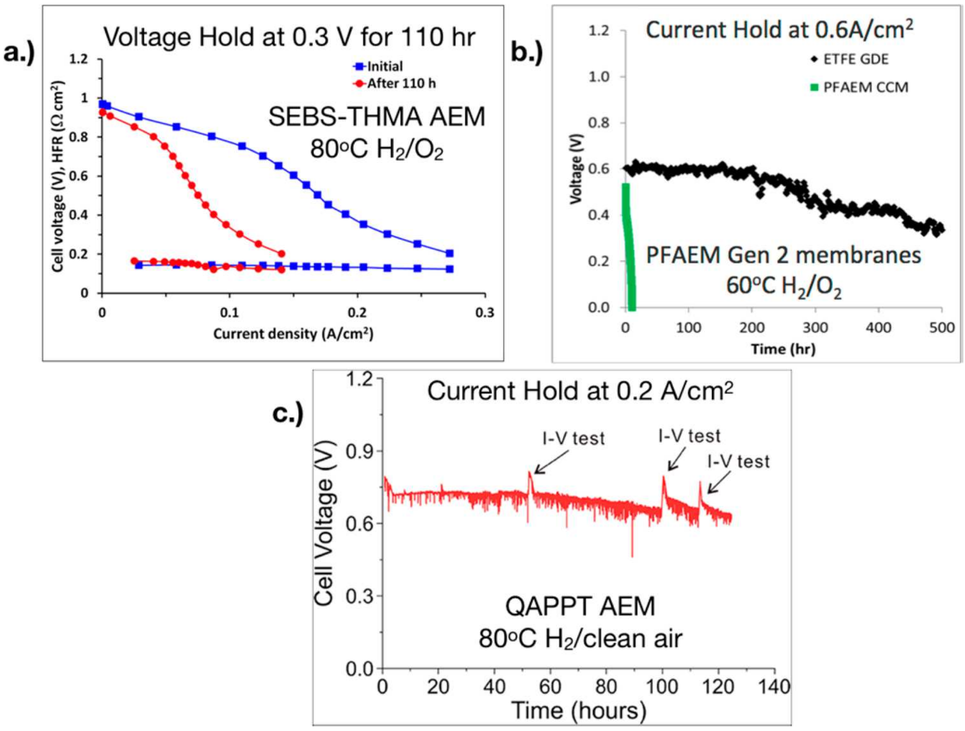

Figure 11. AEMFC device stability tests. (a) SEBS-THMA (quaternary trimethylammonium with *n*-hexyl pendant) based AEM. Adapted with permission from ref 97. Copyright 2015 American Chemical Society. This AEMFC displayed instability as observed by the greater polarization observed after the stability test. However, the stable high frequency resistance value indicated a stable AEM. (b) Perfluorinated AEM with different ionomers used in the electrodes (ETFE quaternary ammonium AEI powder as gas diffusion electrodes versus perfluorinated AEI fabricated into a CCM). From ref 178, U.S. Department of Energy, 2018. The perfluorinated AEM with ETFE quaternary ammonium AEI was relatively stable up to 200 h when operated at 60 °C. (c) QAPPT AEM tested over 125 h with hydrogen and clean air at 80 °C. Adapted with permission from ref 40. Copyright 2018 Elsevier.

workers[96] recently assessed AEMFC stability with a PPO AEM (PPO with *n*-alkyl pendant ammonium groups) that had excellent alkaline resistance versus a PPO AEM with relatively poor alkaline stability (PPO with quaternary benzyl ammonium groups) at higher temperatures. Surprisingly, the inferior alkaline stable PPO AEM had better stability over the alkaline stable PPO AEM. These results call into question whether or not accelerated stress tests in concentrated base baths at elevated temperatures mimic the most relevant degradation modes in AEMFCs.

It is important to mention that U.S. Department of Energy (DOE) has set a technical target of 10% voltage loss or less for a single-cell AEMFC MEA after 2000 h of operation at 600 mA cm^{-2} at a temperature of 60 °C or greater.[93] Similar to alkaline stability protocols of AEMs, no formal testing methodology exists for AEMFCs by a standards organization. In the peer-reviewed literature, stability in the devices has only been assessed up to 300 h (minus the stack results reported by CellEra/Elbit—which reported intermittent operation to 5000 h[90]) and the conditions for stability testing varied widely. Furthermore, the failure modes for loss in cell stability are not typically diagnosed. Because of the recent development of alkaline stable AEMs, more emphasis should be placed on device stability studies rather than just AEM ex situ stability assessments in concentrated base bath.

3.8. Summary of AEM Chemical Stability. To summarize the highlights of the AEM chemical stability section, intense efforts by many groups over the past 5 years have yielded alkaline stable AEMs at elevated temperatures of 80 °C or greater and for hundreds of hours in concentrated base solutions. Table 1 summarizes AEMs with both alkaline stability in 1 M KOH at 80 °C (or greater) for at least 7 days and hydroxide ionic conductivity over 100 mS cm^{-1}. This table includes water uptake/swelling ratio and mechanical properties of the AEMs, as well as known degradation modes in base solutions. Figure 12 gives the chemical structure of these leading AEM candidates summarized in Table 1. The literature review of AEM alkaline stability demonstrates an interplay between the polymer backbone, the tethering linkage, and the cation with regard to the chemical stability of AEMs.[9] Model compound studies do represent a high throughput screening protocol to down select appropriate cation chemistries and tethering linkages to design resilient AEMs in base, but they cannot capture all the other attributes at play that influence AEM stability such as morphology, the role of the polymer backbone, and water content. The monumental gains in AEM maturation derive from not one single researcher, but a cohesive effort by the community to investigate degradation modes with rigor and produce new materials chemistries. Excitingly, multiple chemistries, such as sterically hindered cation groups in the polymer backbone chain[40,99,101,141−143] or pendant ionic groups to *n*-alkyl chains tethered to a polymer backbone,[34,35,37,38,98,100,103−109] yield alkaline stable AEMs—highlighting that multiple strategies exist for achieving alkaline stable AEMs. However, the community cannot rest on their laurels. It needs to evaluate these leading, alkaline resistant AEM candidates in AEMFC device studies. Furthermore, the leading AEM chemistries currently produced in academic and national laboratories are not commercially available. Without a commercially available benchmark AEM, AEMFCs may not

Table 1. Alkaline Stability, Hydroxide Ion Conductivity (σ_{OH-}), Water Uptake/Swelling Ratio, and Mechanical Property Values of Leading AEMs (Shown in Figure 12)

label in Figure 12	membrane name	σ_{OH^-},[a] mS cm^{-1}	alkaline stability[c]	identified degradation mechanism(s)	water uptake/swelling ratio[h]	mechanical properties[j]	ref
a	quaternary ammonium PPO−fluorene *n*-hexylene linker	140	no change in IEC and 7% drop in σ_{OH-} after 41 days[d]	NR	WU, 115% (80 °C); SR, 27% (RT[i])	TS, 16 MPa; EB, 21.7% (hydrated AEM at RT)	34
b	quaternary ammonium poly(biphenyl alkylene)	122	5% change in IEC and no drop in σ_{OH-} after 30 days	NR	WU, 145% (80 °C); SR, 40% (80 °C)	TS, 22 MPa; EB, 45% (50% RH and 50 °C)	103
c	heterocyclic benzyl quaternary ammonium groups grafted to ETFE	159[b]	15% change in IEC after 28 days	cation degradation by debenzylation, ring opening, and dealkylation	WU, 63% (RT); SR, 35% (RT)	TS, 29 MPa; EB, 190% (0% RH and RT)	50
d	poly[9,9-bis(6′-(*N*,*N*,*N*-trimethylammonium)-hexyl)-9*H*-fluorene)-*alt*-(1,4-benzene)]	124	5% change in IEC after 30 days	AEM is fragile after 7 days, but no chemical degradation was detected	WU, 76% (80 °C); SR, 10% (80 °C)	NR	107
e	PPO with cross-linked poly(*N*,*N*-diallyazacycloalkanes) with *N*-spirocyclic quaternary ammonium	101	minor changes observed in ^1H NMR in 2 M KOD/D_2O at T = 120 °C after 14 days	cation degradation by ring-opening or dealkylation	WU: 125% (80 °C)	NR	45
f	PPO AEMs with multiquaternary ammonium *n*-hexylene cross-linker	110	22% change in IEC and 25% drop in σ_{OH-} after 30 days	NR	WU, 101% (RT); SR, 19% (RT)	TS, 20 MPa: EB, 34.4% (hydrated AEM at RT)	42
g	PPO AEM with *n*-pentyl quaternary ammonium pendants using primary amine linkers	96	9% change in IEC and 10% drop in σ_{OH-} after 30 days	NR	WU, 166% (RT); SR, 20% (80 °C)	NR	38
h	polymerized N-spirocyclic quaternary ammoniums (spiron-ionene 2) blended with PBI	115	no changes observed in ^1H NMR in 1 M KOD/D_2O at T = 120 °C after 75 days[f]	cation degradation by ring-opening substitution	WU, 200% (80 °C)	NR	39
i	quaternary ammonium perfluorinated AEM with *n*-hexylene sulfonamide linker	122	10% change in IEC after 14 days	sulfonamide linker degraded in model compounds	WU, 23% (80 °C)	NR	86
j	poly(triarylene) with *n*-hexylene quaternary ammonium pendants	112	2% change in IEC after 60 days[e]	AEM mechanically unstable after use in electrolyzer	WU, 70% (80 °C); SR, 23% (80 °C)	NR	35
k	poly(arylene ether nitrile) with fluorene-*n*-hexylene quaternary ammonium pendants	116	5% change in IEC after 20 days	cation degradation by Hofmann elimination or dealkylaiton	WU, 80% (80 °C); SR, 40% (80 °C)	TS, 38.2 MPa; EB, 7.4% (60% RH and RT)	40
l	quaternary ammonium poly(*n*-methylpiperidine-*co*-*p*-terphenyl)	137	5−18% change in IEC after 210 days[f]	NR	SR, 9.5% (80 °C)	TS, 34.8 MPa; EB, 39.5% (hydrated AEM at RT)	36
m	partially fluorinated poly(arylene ether) with claw-type pendants of quaternary *n*-methylcyclohexyl ammonium groups	98	6% change in IEC and 7% drop in σ_{OH-} after 25 days	NR	WU, 73.2% (80 °C); SR, 15.3% (80 °C)	TS, 15.9 MPa; EB, 18.2% (hydrated AEM at RT)	37

[a] Data were taken at T = 80 °C in liquid water (unless noted otherwise). [b] Data were taken at T = 80 °C at 95% relative humidity. [c] Stability assessment was done at T = 80 °C in 1 M NaOH or 1 M KOH (unless noted otherwise). [d] Alkaline solutions for stability assessment were saturated with argon. [e] T = 95 °C instead of T = 80 °C. [f] ^1H NMR analysis and wet-chemistry titration were used to assess cation stability. Other stability tests were performed in 3 M NaOH, 8 M NaOH, and 10 M NaOH. [g] NR, Not reported. [h] Water uptake and swelling ratio performed for samples in liquid water (unless noted otherwise). Swelling ratio value corresponds to the in plane of the AEM. [i] RT, room temperature [j] Measurement performed at 95% relative humidity and was calculated from the reported λ value (no. of water molecules per ionic groups).

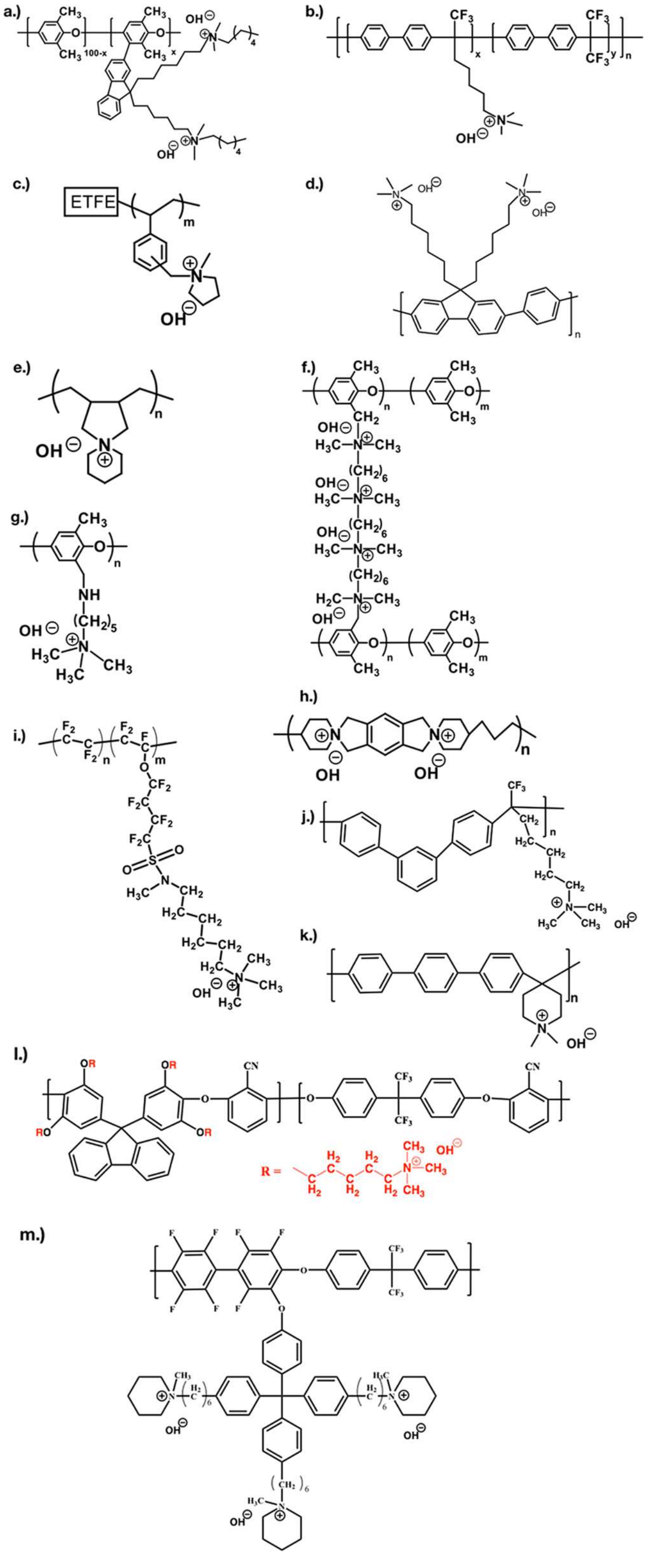

Figure 12. Chemical structures of leading AEMs that exhibit over 100 mS cm^{-1} hydroxide ion conductivity and alkaline stability in 1 M sodium (or potassium) hydroxide (NaOH/KOH) at T = 80 °C with less than 25% degradation. (a) Adapted with permission from ref 34. Copyright 2015 American Chemical Society, (b) Adapted with permission from ref 103. Copyright 2016 American Chemical Society. (c) Reprinted from ref 50. Copyright 2016 – Published by the Royal Society of Chemistry. (d) Adapted with permission from ref 107. Copyright 2015 American Chemical Society. (e) Adapted with permission from ref 45. Copyright 2017 American Chemical Society.

Figure 12. continued

(f) Adapted with permission from ref 42. Copyright 2017 American Chemical Society. (g) Adapted with permission from ref 38. Copyright 2017 American Chemical Society. (h) Adapted with permission from ref 39. Copyright 2017 American Chemical Society. (i) Reprinted from ref86. U.S. Department of Energy, 2017. (j) Adapted with permission from ref 35. Copyright 2018 Elsevier. (k) Adapted with permission from ref 40. Copyright 2018 Elsevier. (l) Adapted with permission from ref 36. Copyright 2018 Elsevier. (m) Adapted with permission from ref 37. Copyright 2018 Royal Society of Chemistry.

realize their full potential as a non-PGM fuel cell technology with desired performance and stability. A commercial manufacturer that can produce one or more of these chemistries at a large scale will catalyze the development of AEMFC devices to match or exceed PEMFC in performance and durability. To close this section, promising AEMs from ex situ stability studies need to be validated in AEMFC devices and also need to demonstrate stability under drier conditions and in the presence of ROS.

4. ANION EXCHANGE IONOMERS AS BINDERS FOR AEMFCS

Anion exchange ionomers (AEIs), which are similar in chemical structure to AEMs, dispersed in the electrode layers of AEMFCs are important to AEMFC performance and stability. Like AEMs, AEIs must also display excellent ionic conduction and longevity in the presence of stringent chemical environments (high pH and strong oxidizing environment). However, AEIs can display notable differences from their bulk membrane counterparts. Karan and co-workers[70,71,179] have shown that thin film (at 100 nm or less) Nafion's ionic conductivity is much smaller and deviates significantly from bulk Nafion membranes. Thin film ionomers are present as binder in the electrode layers of both PEMFCs and AEMFCs. It is not unreasonable to expect that the stability of the AEI may differ from that of the bulk membranes as the electrode may contain different concentrations of ROS and hydroxide ions and water. Furthermore, AEI ionic conductivity as a thin film versus a bulk membrane also differs as seen in the case of Nafion. Two-dimensional layout of thin film Nafion induces confinement that disrupts (or prevents) the microphase separated morphology that is typically present in bulk membranes; therefore thin film Nafions ionic conductivity is hindered. From the alkaline stability perspective, Parrondo and Ramani observed greater degradation of a PPO based AEI in the anode layer versus the cathode layer for an AEM water electrolyzer.[180] This highlights that AEI degradation and stability modes can differ across the MEA in AEMFCs or AEM water electrolyzers.

Another key requirement of AEIs is to dissolve or disperse them into low boiling point solvents for making catalyzed coated membranes (CCMs). However, to successfully apply the ionomer onto electrodes, the solvent that dissolves or disperses the AEI cannot excessively swell or dissolve the same membrane chemistry in the CCM fabrication process. Five years ago, AEMFC power density values transcended from roughly 0.1 to about 0.5 to 1 W cm^{-2} using CCMs.[181−183] High power density AEMFCs are possible without a CCM—as evident by the gas diffusion electrodes with ionomer dispersions (not dissolved ionomer in catalyst inks) used by

Mustain and co-workers.[83,85] To date, they have shown the highest power density for an AEMFC[83] by achieving 1.9 W cm^{-2} with a total platinum group loading less than 1 mg$_{Pt}$ cm^{-2} (using hydrogen and pure oxygen as the oxidant). They have also surpassed 1 W cm^{-2} without a platinum group metal in the cathode.[184] It should be noted that despite the significant gains made in AEMFC performance, the power density gap between AEMFC and PEMFC using air as the oxidant is still quite large. The power density for a PEMFC is greater than 1.3 W cm^{-2} with total platinum loadings of 0.25 mg cm^{-2} at 94 °C and a back-pressure for both gas streams at 250 kPa$_{abs}$ (reported by General Motors in 2016).[185] It should be noted that PEMFCs' performance is not usually judged by peak power density; it is usually assessed by the current density achieved at voltages of 0.7−0.8 V. The best peak power density for an AEMFC with clean air as the oxidant (similar to air but free of carbon dioxide to avoid the carbonation problem) is 0.63 W cm^{-2} at 80 °C and no back-pressure applied—this is with a much larger platinum loading of 0.8 mg cm^{-2} (0.4 mg cm^{-2} at the cathode and anode).[186] Because of the much-placed emphasis to improve AEMs for AEMFCs, there is only a small population of publications solely dedicated to AEIs, but their properties (e.g., ionic conductivity, water uptake, gas permeability, and stability) are vital for moving the AEMFC field forward.

5. SUMMARY AND FUTURE OUTLOOK

The past 5 years of AEM research has yielded new functional material chemistries for AEMFC power sources. Many AEMs display hydroxide ion conductivity values of 100 mS cm^{-1} or greater in flooded cells or under humidified conditions. Additionally, there are alkaline stable AEMs that display excellent resilience in concentrated base baths for hundreds of hours at 80 °C or greater. On top of these stunning achievements, AEMFCs are capable of power densities that surpass 1 W cm^{-2} with hydrogen and oxygen.[85,86,113,182,184] The field, however, cannot stand idle. AEMFCs still need rapid improvement under a robust range of operating conditions, while simultaneously showing long-term fuel cell stability of thousands of hours. This will require AEMs that can conduct, and are stable, under dry conditions in alkaline solutions in addition to being resilient to ROS (e.g., superoxide anion). On top of all that, making AEMFCs a justifiable alternative to PEMFCs requires them to exceed PEMFCs' value proposition in terms of both performance and cost. We hope that this Review will help guide researchers in accomplishing such ambitious goals.

AUTHOR INFORMATION

Corresponding Author

*E-mail: carges@lsu.edu.

ORCID

Christopher G. Arges: 0000-0003-1703-8323

Notes

The authors declare no competing financial interest.

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