

Anion-exchange membranes derived from main group and metal-based cations

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ABSTRACT

The design and synthesis of anion-exchange membranes (AEMs) has attracted a great deal of attention given the potential utility of these materials for ion transport in electrochemical energy systems. AEMs are polymer electrolytes with positively charged groups covalently bound to a polymer backbone that can conduct either hydroxide or other anions. The vast majority of AEMs are based on ammonium groups ($^+NR_4$) but questions surrounding the long-term stability of these functionalities to hydroxide has led to examination of other cation alternatives. In this review, we highlight some of the recent efforts towards AEMs with cations derived from inorganic elements, with a specific emphasis on phosphonium, sulfonium, and metal-based cations. These studies demonstrate the potential of inorganic building blocks for construction of novel AEMs, with unique properties relative to their ammonium analogues.

1. Introduction

Electrochemical devices for energy storage and conversion (e.g. redox-flow batteries, fuel cells, and electrolyzers) all require selective transport of ions under a wide range of conditions, including temperature, pH, and electrochemical stress [1]. Polymers with tethered ionic groups can be used as components in these electrochemical cells, where the bound ions provide pathways to promote charge movement and the backbone acts as structural support [1]. Anionic polymers (e.g. sulfonates) have been successfully used as proton-exchange membranes (PEMs) in a wide range of applications requiring proton transport under acidic conditions [2]. Polymers bearing cationic groups (e.g. quaternary ammoniums) have been used as anion-exchange membranes (AEMs) in applications requiring hydroxide transport, and AEMs continue to be a highly active area of research [3–14]. The pursuit of AEM-based fuel cells and electrolyzers is partially a consequence of the potential use of non-precious electrocatalysts for oxygen reduction and oxygen evolution in alkaline media [9].

The continued search for new AEMs is driven by the necessity to improve both performance and durability of these materials. Ideally, all AEMs would be highly conductive (^-OH conductivities ≥ 100 mS/cm), mechanically robust, and chemically stable at high temperatures in an electrochemical cell (≥ 80 °C). Preparing highly conductive AEMs can be a challenge when compared to PEMs given the lower intrinsic mobility of ^-OH relative to H^+ [15,16]. The long-term chemical stability of AEMs is also a challenge given the nucleophilicity and basicity of caustic

hydroxide. The overwhelming majority of AEM materials studied to date have been based on ammonium cations [3–14], but concern regarding the stability of these cations to alkaline media has prompted investigation of alternative pendant cations in AEMs.

The different classes of cations considered for AEMs can be broadly classified into four categories: organic cations, heavy main-group element cations, organometallic cations, and crown-ether based cations (Fig. 1). Organic cations are derived exclusively from second row elements, such as nitrogen, carbon, and hydrogen. Heavy main-group element cations include at least one element with a principal quantum number ≥ 3 , organometallic cations are derived from transition metals, and the crown-ether cations are derived from the alkali metals. The atoms bearing the positive formal charge are highlighted in yellow in Fig. 1 (only a single resonance form is shown for delocalized cations).

As part of this special issue in honor of Ian Manners (and to recognize his contributions to inorganic polymer chemistry) [17–19], this short review will be focused exclusively on the opportunities and challenges presented by using heavier inorganic elements as building blocks for cationic moieties in AEMs. Brief sections describing phosphonium, sulfonium, organometallic, and crown-ether based AEMs are discussed below. Since the search for novel cations has been primarily to improve durability to hydroxide, reports to date have focused on alkaline stability, synthetic methods to incorporate cations into polymers, and performance as AEMs. Though the physical and mechanical properties of these novel macromolecules is critical to their long-term utility, the bulk of the discussion here is focused on alkaline stability (of model

Abbreviations: AEM, Anion-Exchange Membrane; PEM, Proton-Exchange Membrane.

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compounds where possible), conductivity, water uptake, and ion-exchange capacity (IEC). In addition, though polymer stability in electrochemical cells is also a key aspect, it is not discussed in detail here. Synthetic methods to prepare AEMs fall into two broad categories: direct polymerization (polymerization of cationic monomers) and post-polymerization functionalization (cationic groups are attached to a pre-formed polymer backbone) [4]. Since the synthetic approaches to construct AEMs have been reviewed recently [4], it is not the primary focus of the current review.

Prior to AEM synthesis, assessment of cation stability in alkaline media is ideal [20–23]. Computation can also be used to help identify degradation pathways and barrier heights in the reaction of cations with hydroxide [24–26]. Experimental alkaline stability studies can be carried out in various ways; where the solvent, base concentration, and temperature all have a significant impact on degradation rates (Fig. 2). Generally, a wide range of conditions have been used to examine cation stability, and the variation has been well documented in a recent report on benzyltrimethylammonium degradation [27]. Choice of solvent is important, as solvation of the reactive anion (e.g. OH^-) will impact reactivity and can lead to degradation via different reactive anions (e.g. MeO^- in MeOH) [20]. The Coates group has recently developed a protocol to standardize small molecule degradation studies and enable straightforward comparison of different cation families [20,21]. Any cation (0.03–0.05 M) is combined with either 1 or 2 M KOH/ CD_3OH in a sealed NMR tube and heated to 80 °C for 30 days. Over this time period, rates of degradation are assessed and degradation products are identified using NMR spectroscopy [20,21]. Biphasic reactions ($\text{C}_6\text{H}_5\text{Cl}/\text{NaOH}_{\text{aq}}$) can also be used to rapidly assess alkaline stability in hours, so long as the cation is soluble in the organic phase [23,28].

While protocols have been developed to examine the alkaline stability of cations [20,21], there is still a great deal of variation in how alkaline stability of membranes is evaluated. Pivovar and coworkers recently proposed a standard protocol to examine membrane durability by immersion of an AEM in 1 M KOH at 80 °C for 1000 h, followed by IEC and Cl^- conductivity measurements to quantify cation degradation [29]. The long-term alkaline stability of AEMs is critically important [29], and recent reports have demonstrated that some polymer backbones can chemically degrade in the presence of OH^- [30–32]. Poly(arylene ether sulfone) (PAES) and polyphenylene oxide (PPO) for example, are popular backbone choices for AEMs due to their heat resistance, dimensional stability, and straightforward functionalization, however, it has recently been demonstrated that the aryl ether linkages in PAES and PPO AEMs are susceptible to attack by OH^- (Fig. 3) [30–32]. Though a number of AEM examples in this review are based on PAES and PPO, the chemical stability of the polymer backbone is a key consideration for any novel material to be examined as AEMs. We suspect that future studies on AEMs with tethered inorganic cations will focus more on heteroatom-free polyarylene backbones as well as simple hydrocarbon backbones [32–41].

2. Phosphonium-based AEMs

There are three different sub-classes of phosphonium cations which have been examined in AEMs: alkylphosphoniums, arylphosphoniums, and aminophosphoniums (Fig. 4 – Top). The most common degradation mechanism observed for tetrasubstituted phosphonium hydroxides involves direct attack at the phosphorus atom (Fig. 4 – Bottom) [42]. This proceeds through nucleophilic attack to form a neutral five-coordinate species, followed by subsequent decomposition into a phosphine oxide through deprotonation of the hydroxyl group and elimination of an R^- anion (which rapidly protonates). Studies have demonstrated that this reaction is second order in hydroxide [43], with the rate-determining step being the loss of the R^- anion.

The degradation of phosphonium hydroxides by direct attack is unique when compared to the mechanism for tetraalkylammonium hydroxide degradation (β -H elimination to form an alkene and amine) [42]. The novel degradation pathway for phosphoniums is partially due to the different electronegativities of phosphorus and nitrogen (2.2 vs. 3.0) and the larger coordination numbers that are possible for the heavier group 15 element. Consequently, the design of stable phosphonium cations requires both steric protection around the central atom to prevent direct attack, as well as electronic stabilization of the cation through attachment of electron-donating groups [44,45].

Alkylphosphoniums. Alkyl-substituted phosphoniums were among some of the first cations to be considered as alternatives to ammonium cations in AEMs [46]. Unfortunately, tetraalkylphosphoniums are generally much more susceptible to degradation by hydroxide than the analogous ammonium derivatives. This is best illustrated in Landini's report on stability of phosphonium and ammonium phase-transfer catalysts in the presence of OH^- [28]. Landini and coworkers noted that tetrabutylphosphonium chloride ($\text{PBu}_4[\text{Cl}]$) had a half-life of only 0.03 h at 25 °C in $\text{C}_6\text{H}_5\text{Cl}/50$ wt % NaOH, while the ammonium analogue ($\text{NBu}_4[\text{Cl}]$) had remarkably better stability, with a half-life of 18 h under identical conditions [28]. Given Landini's observations, it is unlikely that tetraalkylphosphonium polymers will be able to maintain the alkaline stability necessary for OH^- transport applications. Nevertheless, several alkylphosphonium AEMs have been synthesized via quaternization of aromatic polymers with pendant electrophiles using either trimethylphosphine (TMP) or tributylphosphine (TBP).

One of the first phosphonium-functionalized polymers to be examined as an AEM was derived from poly(arylene ether sulfone), abbreviated here as PAES [46]. PAES can be chloromethylated using paraformaldehyde, trimethylchlorosilane, and stannic chloride [46], where the degree of chloromethylation can be controlled by reaction time [47]. Up to two aryl rings in each repeat unit can be functionalized using this approach, which is typically noted as 200% degree of functionalization. Conversion of the chloromethyl groups to cationic groups is then accomplished by reaction with a suitable nucleophile. Poly(ether ether ketone) (PEEK) can also be functionalized in a similar manner to the PAES. PAES or PEEK AEMs are depicted in figures with a single cation appended to the chain, with percent functionalization noted

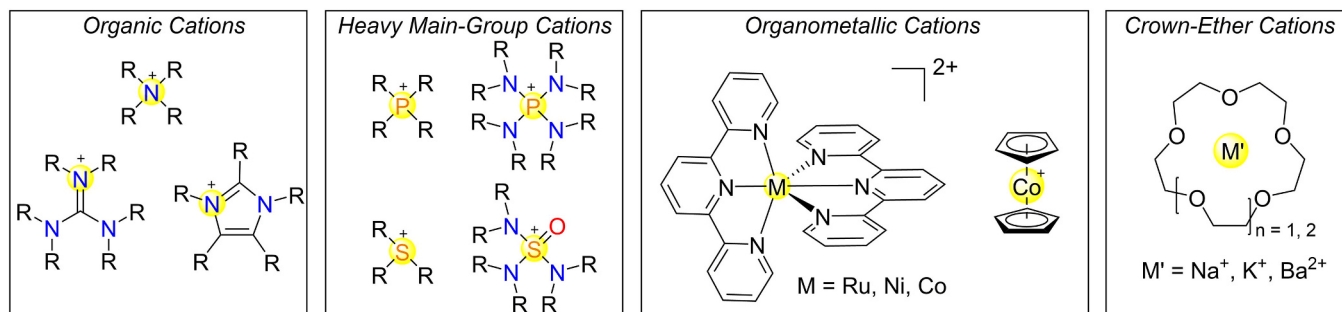


Fig. 1. Classes of cations explored in AEMs.

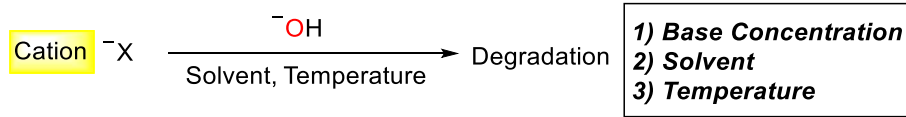


Fig. 2. Parameters that will influence degradation of cations in alkaline media.

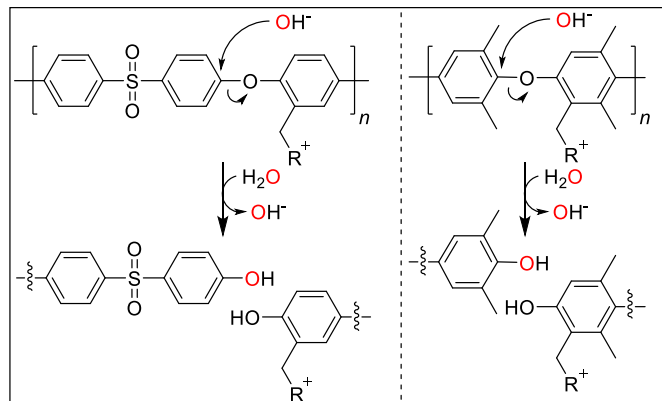


Fig. 3. ^-OH promoted degradation of poly(arylene ether) backbones with appended cationic groups [30–32].

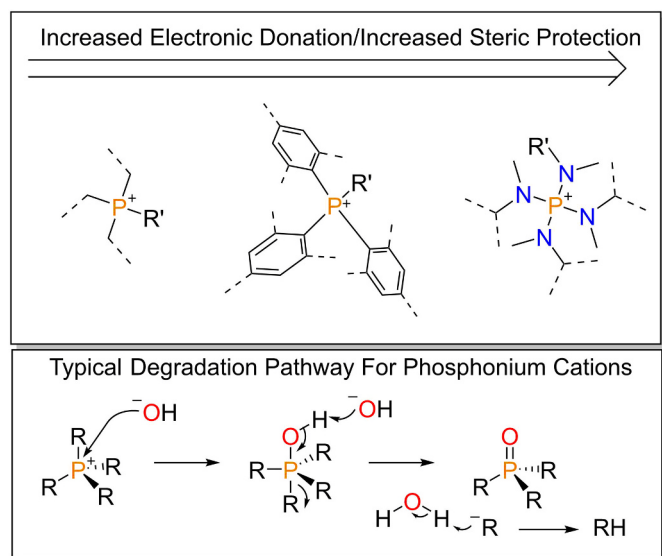


Fig. 4. (Top) Phosphonium cations examined in AEMs. The R' group denotes the tethering point to the polymer and the dotted bonds correspond to sites where synthetic modification can potentially be used to improve alkaline stability. (Bottom) Most commonly observed degradation pathway for phosphonium cations.

(Fig. 5).

Ramani and coworkers synthesized a series of chloromethylated PAES polymers and converted them into benzyltrimethylphosphonium-based AEMs by reaction with TMP (Fig. 5 – PAES-TMP) [46,48]. The Cl^- conductivities were high for the PAES-TMP polymers, with one derivative having a conductivity up to 50 mS/cm at 70 °C (IEC of 1.91 mmol/g). Unfortunately, ^-OH conductivity measurements for PAES-TMP were impossible due to instability upon immersion in 1 M KOH for 24 h [46]. This instability to ^-OH is a common theme among TMP-based AEMs, and was also noted by Elabd and coworkers in their synthesis of TMP-functionalized polystyrene via reversible addition-fragmentation chain-transfer polymerization (RAFT) (Fig. 5 –

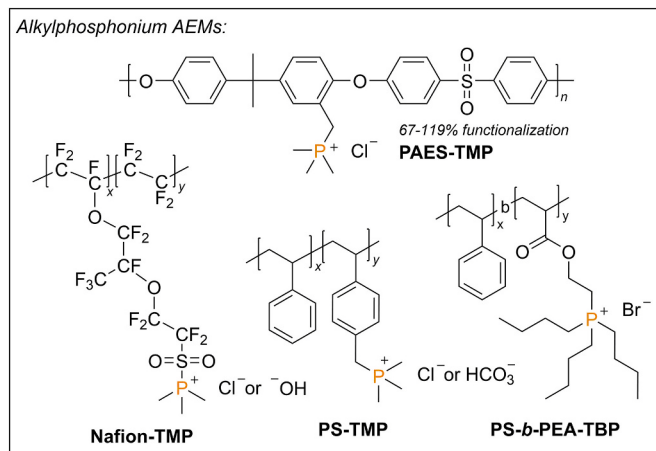


Fig. 5. Summary of alkylphosphonium polymers examined as AEMs.

PS-TMP) [49]. Though Cl^- and HCO_3^- conductivity of PS-TMP could be measured, the films degraded extensively upon exchange to the ^-OH form [49]. In a notable exception, a TMP-based Nafion was synthesized via the attachment through the $-\text{CF}_2\text{SO}_2-$ side group to make an AEM with a ^-OH conductivity between 2.6 and 8.4 mS/cm from 30 to 80 °C (Fig. 5 – Nafion-TMP). Though ^-OH conductivity could be measured, the membrane degraded entirely after 24 h in 1 M KOH at 80 °C [50].

One unique example of an alkylphosphonium AEM reported by Balsara and coworkers involved quaternization of poly[(styrene)-*b*-(bromoethyl acrylate)] with tributylphosphine (Fig. 5 – PS-*b*-PEA-TBP) [51]. The authors demonstrated that these copolymers self-assemble into lamellae with tunable domain sizes by changing the molecular weight of the diblock, as evidenced by small-angle X-ray scattering studies [51]. The authors noted a remarkable increase in Br^- conductivity with increased domain spacing; where an increase in d spacing from 26 to 63 nm led to an increase in conductivity from 6 mS/cm to 21 mS/cm [51]. This important result demonstrates the remarkable changes in AEM performance that are possible with control over polymer morphology. The hydroxide conductivity and alkaline stability of PS-*b*-PEA-TBP was not examined, likely due to the anticipated instability of the material.

Arylphosphoniums. Tetraarylphosphoniums (e.g. tetraphenylphosphonium) are also known to degrade primarily via direct attack at phosphorus, similar to alkylphosphonium cations [52]. Yan and coworkers synthesized a series of benzyl(triaryl)phosphonium model compounds to investigate how electron-donating substituents on the phenyl group impacted cation decomposition rates and pathways in 1 M KOD $\text{CD}_3\text{OD}/\text{D}_2\text{O}$ (5:1 v/v) at 80 °C (Fig. 6) [53]. For benzyl(triphenyl)phosphonium, a decomposition rate could not be determined as triphenylphosphine oxide formed rapidly at room temperature [53]. Notably, methoxy groups on the *para* positions of the arene markedly enhanced cation stability, with a rate constant of degradation at 80 °C (k_{80}^{-1}) of $1.3 \times 10^{-3} \text{ s}^{-1}$ [53]. Complete *ortho/para* functionalization with methoxy groups further reduces the degradation rate by several orders of magnitude ($k_{80}^{-1} = 4.0 \times 10^{-7} \text{ s}^{-1}$) [53]. This is likely due to both the steric protection and the increased donor power of the aryl rings to stabilize the electron deficient phosphorus atom. However, tris (2,4,6-trimethoxyphenyl)phosphonium is susceptible to an alternative

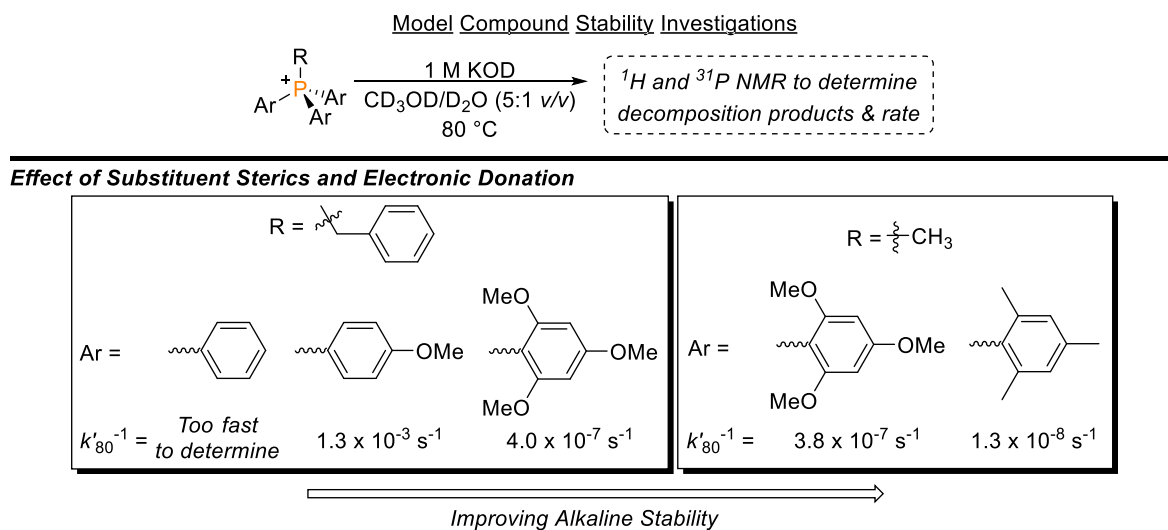
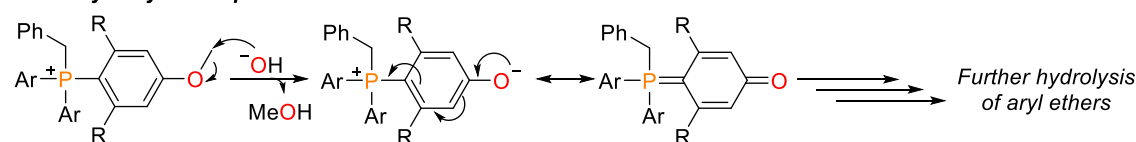
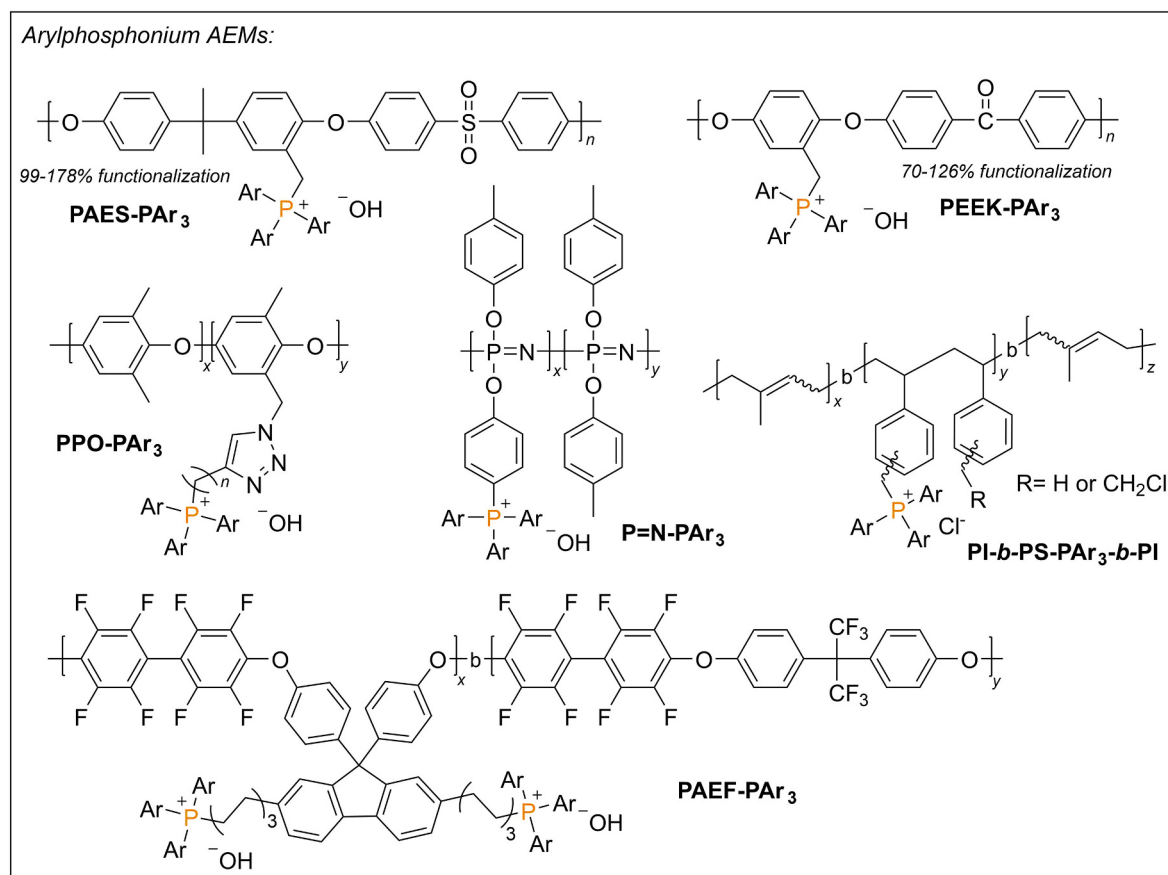
**Ether Hydrolysis Proposed Mechanism**

Fig. 6. Alkaline stability studies for arylphosphonium cations [53].

Fig. 7. Summary of arylphosphonium polymers examined as AEMs. The Ar group attached to phosphorus is typically 2,4,6-trimethoxyphenyl, but in the polyphosphazene example, the Ar groups are either phenyl, 4-(methyl)phenyl, 4-(methoxy)phenyl, or 4-(*t*-butyl)phenyl.

degradation pathway. Rather than direct OH^- attack to form a phosphine oxide, Yan and coworkers observed exclusive formation of degradation products consistent with ether hydrolysis (Fig. 6) [53]. Replacement of the methoxy groups with methyl groups prevents this mechanism while further reducing the degradation rate ($k'_{50} = 1.3 \times 10^{-8} \text{ s}^{-1}$) [45,53].

Most arylphosphonium-based AEMs are synthesized via nucleophilic displacement of an alkyl or benzyl halide with tris(2,4,6-trimethoxyphenyl)phosphine (TTMPP). Yan and coworkers initially reported a TTMPP-substituted PAES AEM with OH^- conductivity of 45 mS/cm at room temperature and 137% water uptake [54]. This material was reported to be stable in 1 M KOH at 60 °C for 1 month (Fig. 7 – PAES- PAR_3) [54]. Cross-linking has been used to significantly reduce swelling of these PAES- PAR_3 polymers in water [55,56]. In a similar fashion, He and coworkers synthesized a TTMPP-based PEEK AEM with OH^- conductivities of 61–89 mS/cm between 20 and 60 °C (IEC of 1.19 mmol/g), though the water uptake for the polymer reached 389% at high temperatures (Fig. 7 – PEEK- PAR_3) [57]. PPO phosphoniums have also been synthesized, either through phosphine substitution onto a brominated PPO or via azide-alkyne cycloaddition of an alkyne-substituted TTMPP cation, forming the polymer shown in Fig. 7 (PPO- PAR_3) [58,59]. An optimized derivative of PPO- PAR_3 had OH^- conductivity of 15.8 mS/cm at 20 °C with an IEC of 0.91 mmol/g, and these derivatives were noted to lose only 10% of their bicarbonate conductivity after soaking in 10 M NaOH at 80 °C for 200 h [58]. A TTMPP multiblock copoly(arylene ether) synthesized by Liu and Kohl had OH^- conductivities of 14.2 – 46.1 mS/cm between 25 and 80 °C (Fig. 7 – PAEF- PAR_3) [60]. The unique fluorinated poly(arylene ether) backbone likely contributed to the phase segregated morphology in these systems [60]. The PAEF- PAR_3 membrane had only 22% water uptake with an IEC of 0.87 mmol/g, which could be a result of the hydrophobic backbone [60]. Limited swelling in water is ideal, as this prevents significant dimensional changes to the material in electrochemical devices.

Beyond polyether backbones, Coughlin and coworkers synthesized TTMPP-functionalized di- and triblock copolymers of polyisoprene and polystyrene (Fig. 7 – PI-*b*-PS- PAR_3 -*b*-PI) [61]. The Cl^- conductivities of these polymers were measured, with the highest being 20.6 mS/cm at 90 °C (IEC 0.45 mmol/g) [61]. The authors noted that low volume fractions of ionic blocks resulted in lamellar morphologies, whereas moderate volume fractions of the ionic blocks resulted in hexagonal phases and higher conductivities ($\geq 30\%$ for triblock and $\geq 22\%$ for diblock copolymers) [61]. In a unique example, Han et al. were able to append various arylphosphonium cations to a polyphosphazene backbone, with OH^- conductivities ranging from 10 to 20 mS/cm from 30 to 80 °C (Fig. 7 – P=N- PAR_3) [62]. Water uptakes for these

polyphosphazenes were less than 15%, which is excellent for dimensional stability [62]. Unfortunately, IEC in these polymers could not exceed ~ 0.75 mmol/g, with the authors hypothesizing that steric hindrance caused by the bulky phosphoniums likely prevented high degrees of substitution [62].

Aminophosphoniums. Aminophosphoniums have also been explored as cationic groups for AEM use. These types of cations were first synthesized in the 1980's [63,64], and the series was expanded upon in 2006 [44]. Both research teams noted the exceptional stability of these cations to alkaline media [44,64], which can be partially attributed to delocalization of the positive charge via the attached nitrogen atoms. The specific choice of amino groups can also significantly impact stability, as these substituents provide steric protection to prevent attack at the phosphorus atom [44]. Schwesinger and coworkers demonstrated that dialkylaminophosphoniums with 2° alkyl groups were exceptionally stable to alkaline media (Fig. 8) [44]. For example, $\text{P}(\text{NMe}_2)_4[\text{Cl}]$ had a half-life of only 0.33 h at 100 °C in $\text{C}_6\text{H}_5\text{Cl}/50 \text{ wt } \% \text{ NaOH}$, while the $\text{P}(\text{N}(\text{iPr})\text{Me})_4[\text{Cl}]$ had a half-life of 6 h under identical conditions [44]. Stability can be further improved by replacing the isopropyl group with a 3-pentyl group or cyclohexyl group [23], as these groups further limit hydroxide attack at the central phosphorus atom.

While aminophosphoniums can be more alkaline resistant than ammonium cations, only a few reports have appeared on aminophosphonium AEMs. One of the first examples to appear in the literature was from the Verkade group, where the proazaphosphatranium derived from tris(2-aminoethyl)amine was appended to Nafion via the pendant $-\text{CF}_2\text{SO}_2-$ side group (Fig. 9 – Nafion-Verkade) [65]. Though AEM performance metrics were not measured for this material, the use of compact aminophosphonium bases is an area worthy of further exploration. A similar Nafion-based AEM (Fig. 9 – Nafion-*t*-BuP1) was made by Arges et al. with a promising 20 mS/cm OH^- conductivity at 80 °C [46].

The first aminophosphonium polyolefin AEM was synthesized by Coates and coworkers [66]. The exceptional stability of the bulky $\text{P}(\text{N}(\text{Cy})\text{Me})_4[\text{Cl}]$ as a phase-transfer catalyst under alkaline conditions ($t_{1/2} = 67 \text{ h}$ at 100 °C in $\text{C}_6\text{H}_5\text{Cl}/50 \text{ wt } \% \text{ NaOH}$) [44], inspired the synthesis of a polyethylene AEM with this cation appended to the backbone (PE-CyMe in Fig. 9). PE-CyMe was prepared by copolymerization of a phosphonium-functionalized cyclooctene and cyclooctene using ring-opening metathesis polymerization (ROMP), followed by hydrogenation [66]. The room temperature OH^- conductivity for this copolymer was 22 mS/cm with moderate 52% water uptake [66]. The conductivity value for this material was fairly high given the low measured IEC value (0.67 mmol/g), and PE-CyMe proved to be exceptionally stable to alkaline media, with no significant loss of conductivity after exposure of the material to 15 M KOH at 22 °C for 20 weeks [66].

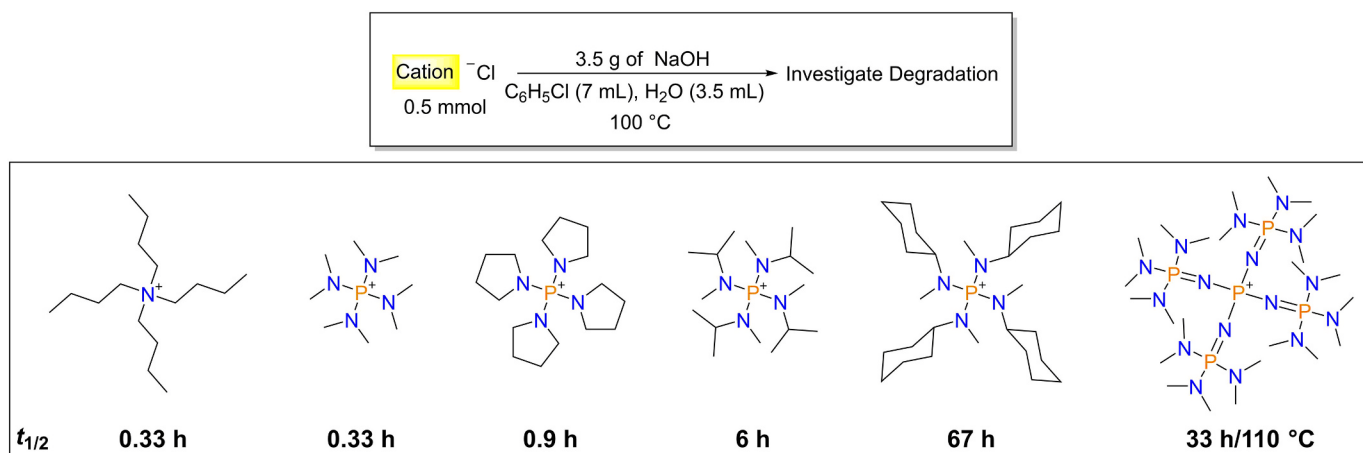


Fig. 8. Half-life data for select dialkylaminophosphonium phase transfer catalysts in biphasic reactions, as reported by Schwesinger and coworkers in Ref. [44].

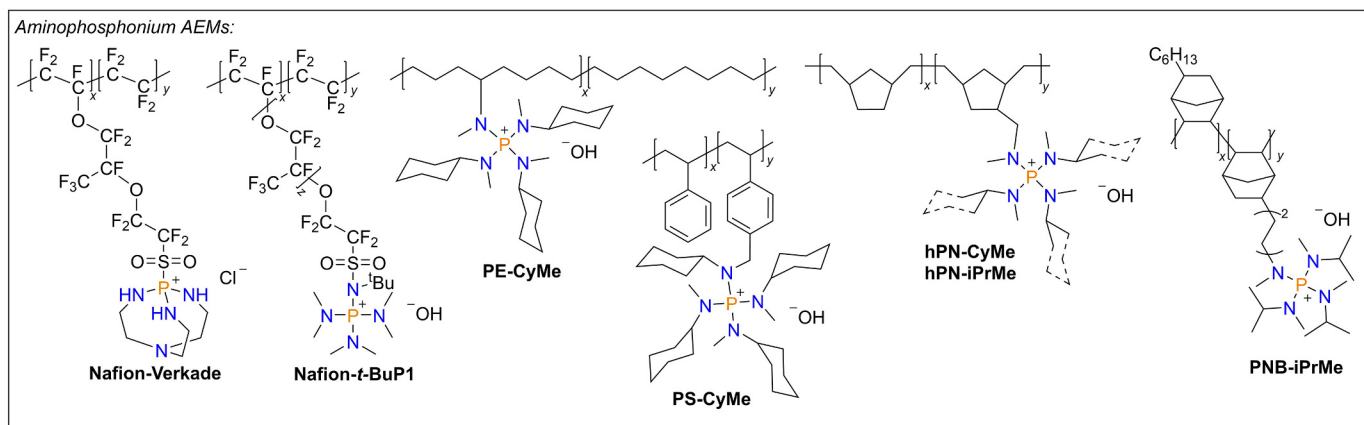


Fig. 9. Summary of aminophosphonium polymers examined as AEMs.

The fairly complicated synthesis of PE-CyMe led to exploration of a CyMe-functionalized polystyrene which could be readily synthesized [67], but the resultant PS-CyMe (Fig. 9) was too brittle for conductivity measurements [67].

Polynorbornenes have also been recently examined as backbones with aminophosphonium cations (hPN-CyMe, hPN-iPrMe, and PNB-iPrMe in Fig. 9) [68,69]. Ring-opened polynorbornenes could be synthesized by copolymerization of a phosphonium-functionalized norbornene with norbornene, where hPN-CyMe had a OH^- conductivity of 19 mS/cm at 25 °C and 82% water uptake [68]. By moving to the more compact tris(isopropylmethylamino)phosphonium cation (hPN-iPrMe), the OH^- conductivity could be improved to 27 mS/cm at 25 °C and 43 mS/cm at 80 °C (IEC $\sim$ 0.8 mmol/g and water uptake $\sim$ 86%) [68]. For all three aminophosphonium copolymers synthesized using ROMP (PE-CyMe, hPN-CyMe, and hPN-iPrMe), targeting phosphonium concentrations of 20 mol % or higher was not possible without excessive swelling, which ultimately limited the conductivity of these materials [66,68]. Recently, it was noted that a vinyl addition polynorbornene could help decrease the swelling observed for aminophosphonium AEMs (Fig. 9 – PNB-iPrMe). The rigid backbone was effective in lowering the water uptake to 59% for a statistical copolymer with an IEC of 1.12 mmol/g [69]. The OH^- conductivity observed for PNB-iPrMe (52 mS/cm at 80 °C) is one of the highest for the aminophosphonium materials [69]. Though no stability studies were performed on PNB-iPrMe, the stability of $\text{P}(\text{N}(\text{iPr})\text{Me})_4[\text{Cl}]$ as a phase-transfer catalyst [44] in combination with the polyolefin backbone is likely to confer good resistance to hydroxide attack for these systems. Tetraalkylammonium polynorbornene AEMs have previously been reported to exhibit excellent alkaline stability, losing less than 2% of their hydroxide conductivity upon immersion in 1 M NaOH at 80 °C for 1000–1200 h [70–72].

3. Sulfonium-based AEMs

Sulfonium cations are like their phosphonium counterparts, where alkyl, aryl, or dialkylamino groups can be bound to the sulfur atom (Fig. 10). Oxidation of the 3-coordinate sulfonium species to afford cationic sulfoxoniums is also a possibility (Fig. 10). Sulfonium cations have received limited attention [73,74], and no sulfoxonium cations have appeared in AEMs to our knowledge. Alkylated sulfur cations, such as trimethylsulfonium and trimethylsulfoxonium, are known to readily react with bases to form sulfonium ylides [75,76]. Given this, these derivatives are unlikely to be effective cations for hydroxide-based AEMs. Triphenylsulfonium cations have also been reported to degrade in the presence of both hydroxide and alkoxides, either through direct attack at the sulfur atom or on an attached aryl group [77,78]. It may be possible to improve the alkaline stability of these motifs using a similar approach to that used for stabilizing arylphosphoniums, as described by

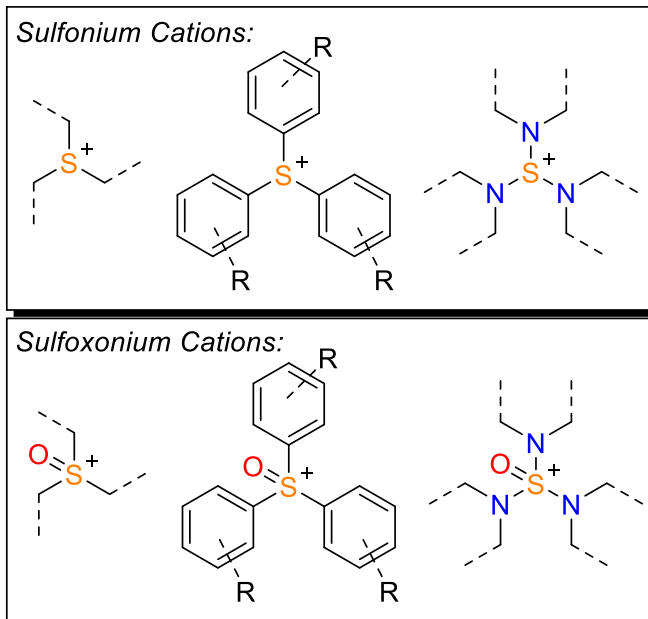


Fig. 10. Sulfur-based cations where the dotted bonds correspond to possible points of synthetic modification to improve alkaline stability.

Yan and coworkers [45,53].

Some of the most exciting potential sulfur cation candidates for exploration in AEMs are the tris(dialkylamino)sulfoniums and sulfoxoniums $[\text{S}(\text{NR}_2)_3]^+$ and $[\text{O}=\text{S}(\text{NR}_2)_3]^+$ shown in Fig. 10 [79,80]. These compounds are related to $[\text{P}(\text{NR}_2)_4]^+$ compounds where the nitrogen and oxygen atoms attached to the central sulfur atom enable delocalization of the cationic charge. The amino groups also enable straightforward tuning of the steric environment around the sulfur center. Kobayashi and coworkers have reported that tris(dialkylamino)sulfoxonium cations are particularly resistant to reaction with nucleophiles and only react under drastic conditions [79]. For example, the authors noted that tris(morpholino)sulfoxonium reaction with $[\text{Na}][\text{CH}_2\text{S}(\text{O})\text{CH}_3]$ was accomplished only at 150 °C, with conversion to the 4, 4'-finyldimorpholine which degrades further to a simple morpholinium salt [79]. These results suggest $[\text{O}=\text{S}(\text{NR}_2)_3]^+$ motifs are exciting candidates for potential use in AEMs.

To date, only two sulfonium-based AEMs have appeared in the literature, both derived from a PAES backbone [73,74]. Chloromethylation of PAES followed by reaction with dimethylsulfide afforded PAES-SR₃ [74], while PAES-SAR₃ was prepared in two steps from the

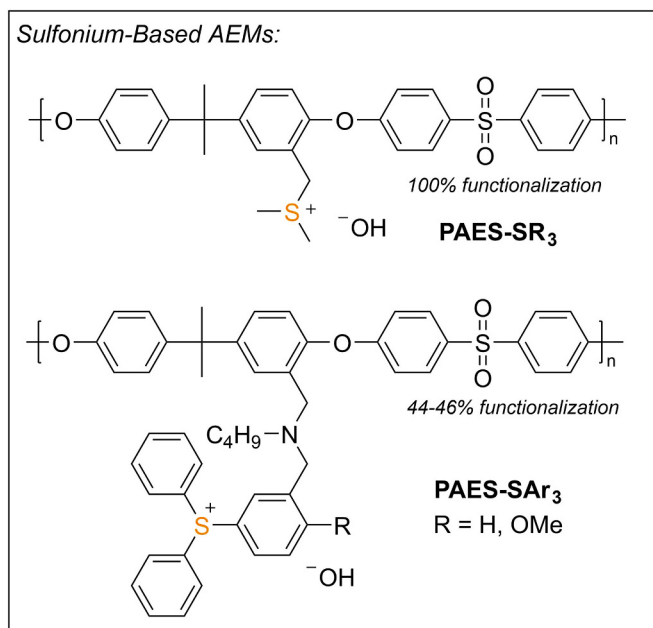


Fig. 11. Sulfonium-functionalized polymers examined as AEMs.

chloromethylated PAES (Fig. 11) [73]. PAES-SR₃ had a ⁻OH conductivity of 15.6 mS/cm at 80 °C and only 16% water uptake (IEC 1.4 mmol/g) [74], while the methoxy-substituted triarylsulfonium (PAES-Sar₃ where R = OMe) had nearly the same conductivity (15.4 mS/cm) but at room temperature [73]. The methoxy group was found to be important to PAES-Sar₃ stability, as the PAES-Sar₃ with the OMe group was stable in 1 M KOH/D₂O at 60 °C for 10 days [73]. Under identical conditions, the PAES-Sar₃ without the methoxy group (R = H) degraded completely, illustrating the importance of electron donation from the arenes to the sulfonium, similar to the observations with arylphosphoniums [45,53].

4. Metal-based cations

In recent years, metal-based cations have begun to attract attention in AEMs due to their unique properties. Metal cations can carry a 2+ charge, allowing for more anions per cationic monomer [81]. In addition, degradation of transition metal cations can be examined using UV-Vis spectroscopy in some instances [81–83]. When designing metal-based cations, redox potentials must be considered for compatibility with the operational window of an AEM fuel cell [83]. To date, a few cationic metals have been explored in AEMs (Co, Ru, Ni, or alkali metals) with either cyclopentadienyl or terpyridine ligands. The examination of these types of cations is still in its infancy with only a few reports to date.

5. Cobalt-based AEMs

The majority of AEM materials with cobalt cations are based on cobaltoceniums (Cp₂Co⁺), where the strong metal-ligand bonds limit nucleophilic attack by ⁻OH at the metal center [84]. The straightforward derivatization of cyclopentadienyl (Cp) ligands also enables tuning of the steric and electronic environment around the metal center to improve alkaline stability. In 2015, Coughlin and coworkers compared cobaltocenium and decamethylcobaltocenium (Cp₂Co⁺ and Cp^{*}₂Co⁺) cations utilizing theoretical calculations and alkaline stability studies [84]. The heat of formation for Cp^{*}₂Co⁺ was computed to be ~36% lower than Cp₂Co⁺ (499 vs. 775 kJ/mol), which suggests Cp^{*} ligands bond to the metal center more strongly than unsubstituted Cp [84]. Gas phase heats of formation for Cp^{*}₂Co⁺ and Cp₂Co⁺ were calculated using semiempirical approaches with MOPAC2012 [84]. The same set of

calculations also revealed a lower charge on cobalt in Cp^{*}₂Co⁺ than in Cp₂Co⁺ (+0.988 vs + 1.058 e, 6.6% reduction), which was expected to enhance cation durability in the presence of ⁻OH [84].

Base stability studies at 140 °C in 1 M NaOD/D₂O confirmed that Cp^{*}₂Co⁺ was markedly more alkaline stable than Cp₂Co⁺ (Cp^{*}₂Co⁺ was ~8.5% degraded after 1000 h, Cp₂Co⁺ was 100% degraded after ~170 h) [84]. In more recent studies, additional evidence confirmed that alkaline stability of cobaltoceniums could be improved by alkyl substitution on the Cp rings [83,85]. Tang and coworkers illustrated how increasing the number of methyl groups on each of the Cp rings increased resistance to base attack (compounds 1 to 2c in Fig. 12), and that up to two *tert*-butyl groups on each Cp ring can lead to enhanced stability (3a – 3b in Fig. 12) [83].

The most alkaline stable derivatives identified in Tang's study, the octamethyl cobaltocenium (2c) and tetra-*t*-butyl cobaltocenium (3b), degraded by only 18.5% and 8.2% after ~1025 h in 5 M KOH/CD₃OH at 80 °C (Fig. 12) [83]. These substituted cobaltocenium derivatives are markedly more stable than benchmark compounds like benzyltrimethylammonium (4) and benzyl tetramethylimidazolium (5). However, reduction of 3b (Co³⁺ to Co²⁺) was noted within the potential window for the hydrogen oxidation reaction at the anode (–828 mV vs Standard Hydrogen Electrode/SHE). In light of the exceptional alkaline stability and electrochemical reduction beyond –1 V, the authors focused on derivative 2c from this series for exploration in AEMs [83].

The first example of a cobaltocenium AEM was synthesized by Coughlin, Yan, and coworkers, who synthesized AEMs bearing either Cp₂Co⁺ or Cp^{*}₂Co⁺ cations on PAES via a diamine linker (Fig. 13 – PAES-Cp^{*}₂Co) [84]. The Cp^{*}₂Co⁺ film had a ⁻OH conductivity of 64 mS/cm at 80 °C (IEC of 1.16 mmol/g, 68% water uptake), however, soaking the material in 1 M KOH at 100 °C led to a 50% loss in IEC after 2000 h [84]. Since the initial report, a variety of cobaltocenium AEMs have been synthesized via direct polymerization using ROMP [82,83,86, 87]. In one example, Tang and coworkers synthesized a Cp₂Co⁺ AEM with a polyethylene backbone (Fig. 13 – PE-Cp₂Co) which had a 90 mS/cm ⁻OH conductivity at 90 °C and water uptake ranging from 35 to 160% between 20 and 80 °C (IEC = 1.86 mmol/g) [82]. To take advantage of the improved alkaline stability of substituted cobaltoceniums, the same group incorporated octamethylcobaltocenium into an AEM (Fig. 13 – PE-Cp₂(Me)Co) [83]. For a polymer with half the ionic content, the ⁻OH conductivity of PE-Cp₂(Me)Co (83.7 mS/cm at 80 °C) was still comparable to PE-Cp₂Co, likely owing to the near threefold reduction in water uptake [83]. These polymers could also be cross-linked to mitigate swelling in water [86]. Another ROMP-based AEM, PN-Cp₂Co (Fig. 13), had a Cl⁻ conductivity of 50 mS/cm at 90 °C and only 13.2% water uptake for a polymer with an IEC of 1.5 mmol/g [87].

Cobaltocenium cations may also be incorporated as a part of the polymer backbone, as in the example by Chen et al., who synthesized a variety of poly(benzimidazole)-based AEMs [85]. The highest performing PBI-Cp₂Co AEM (Fig. 13 – PBI-Cp₂Co) had a ⁻OH conductivity of 37.5 mS/cm at 90 °C and only 40% water uptake for a film with a rather high IEC value of 1.92 mmol/g [85]. When immersed in 1 M KOH at 60 °C, ⁻OH conductivity decreased 15–20% over 672 h, which may be attributed to ring-opening of the benzimidazole backbone, along with possible cation degradation [85]. A single example of a bis(terpyridine) Co²⁺ was examined by Kwasny and Tew, however, the cobalt-based AEM was outperformed by the identical Ru and Ni-based membranes, having a Cl⁻ conductivity of only 0.3 mS/cm at 80 °C (Fig. 13 – PN-xlinked-Tpy₂Co) [88].

6. Ruthenium-based AEMs

The relative scarcity and expense of ruthenium metal may limit its use as a pendant functionality for ion transport [88], though promising work has been carried out to evaluate its potential in AEMs. The [bis(terpyridine)Ru(II)]²⁺ was hypothesized to be a good pendant group for anion-exchange materials due to its well-known thermal and chemical

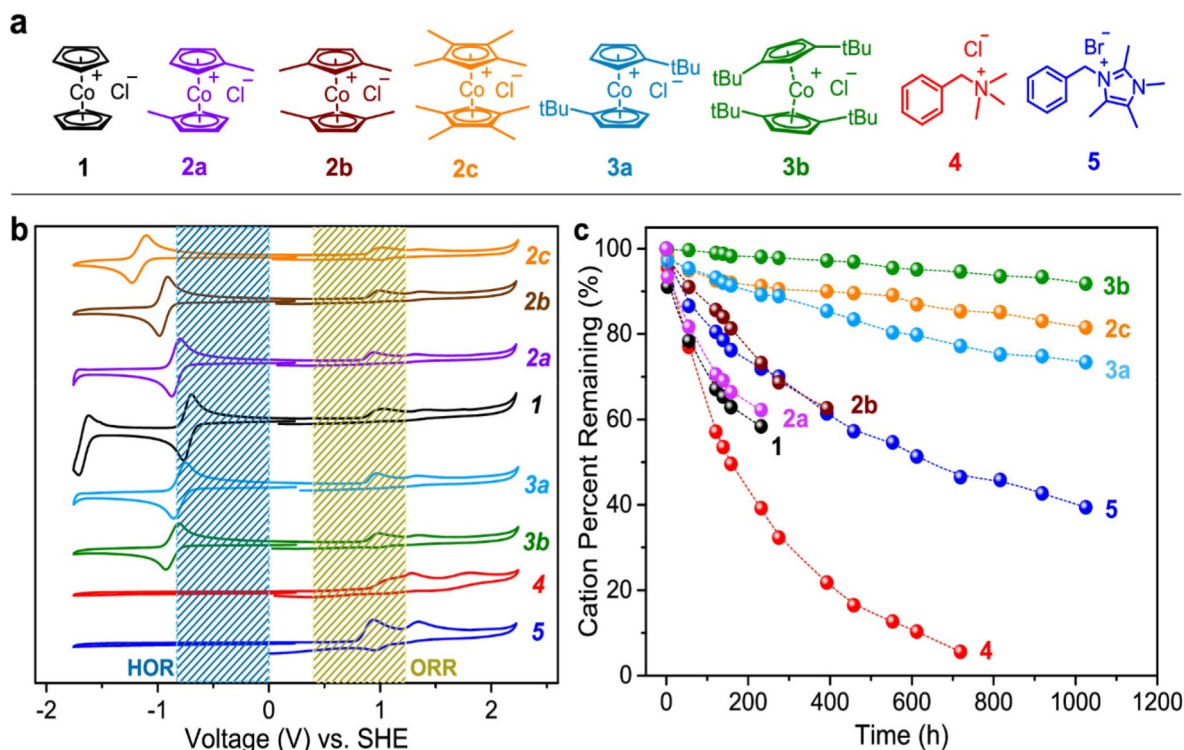


Fig. 12. Left - cyclic voltammograms collected at a scan of 100 mV/s in CH₃CN with 0.1 M NBu₄PF₆ as the supporting electrolyte. Shadows represent HOR and ORR potentials. Right - alkaline stability studies of cations 1–5 (0.025 M) in 5 M KOH/CD₃OH at 80 °C under air. Reproduced with permission from Ref. [83].

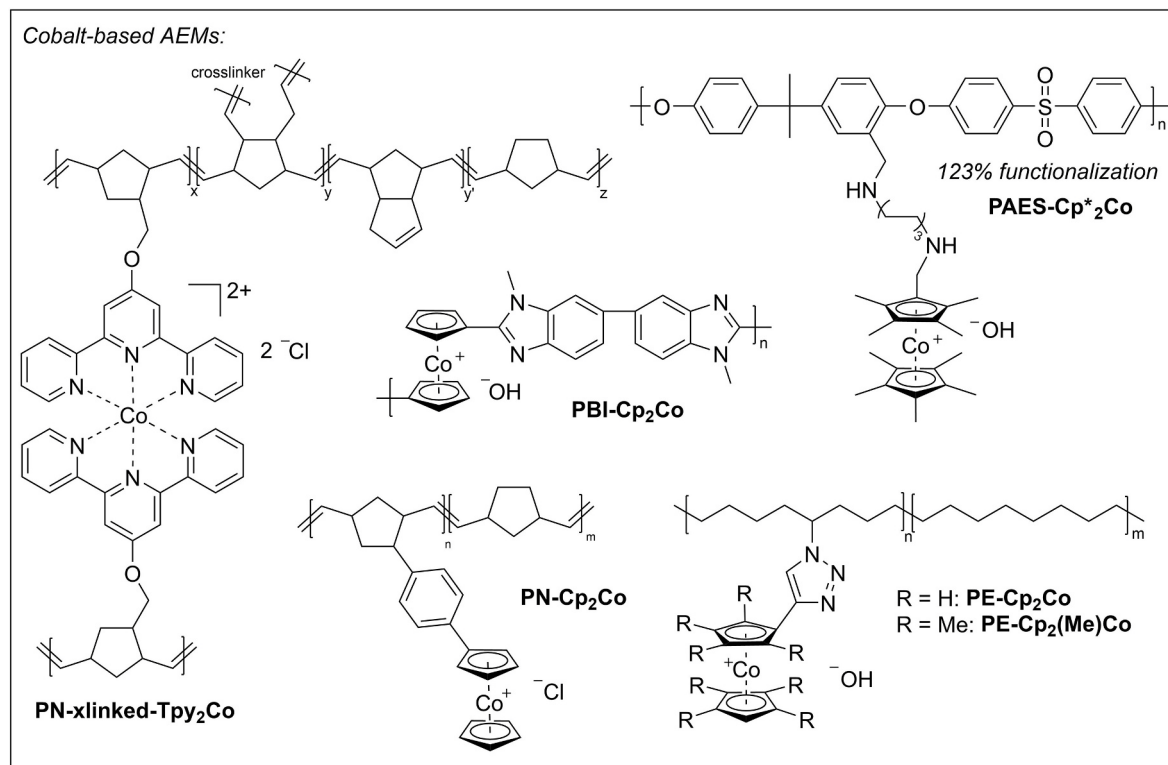


Fig. 13. Cobalt-based polymers examined as AEMs.

stability in aqueous environments up to 70 °C and pH 14 [89]. An additional benefit of the ruthenium complex is the 2+ charge, allowing for the association of two anions per metal center. In terms of practical use, it has been reported that the redox potentials for this cation are

outside of the window of fuel cell operation, suggesting sufficient electrochemical stability [81].

Hickner, Tew, and coworkers noted that a norbornene-functionalized [bis(terpyridine)Ru(II)]Cl₂ was stable in 1 M NaOH at

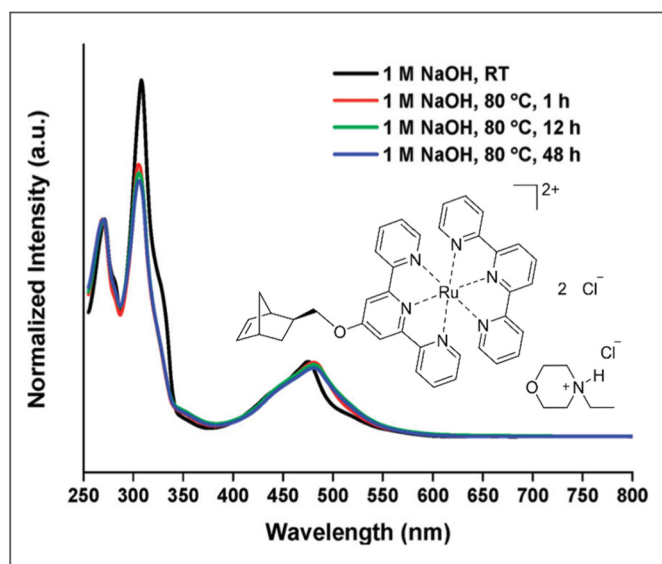


Fig. 14. $[\text{bis(terpyridine)Ru(II)}]^{2+}$ monomer and corresponding UV-Vis spectrum of the monomer after exposure to 1 M NaOH at room temperature and 80 °C. Adapted from Ref. [81].

room temperature for 6 months, as minimal changes were noted in the UV-vis spectra for the complex [81]. The same complex was also shown to be stable in 1 M NaOH at 80 °C for 48 h with minimal change to the UV-vis spectra over that timeframe (Fig. 14) [81]. The norbornene-functionalized $[\text{bis(terpyridine)Ru(II)}]\text{Cl}_2$ was copolymerized with dicyclopentadiene to afford a cross-linked network as shown in Fig. 15 (PN-xlinked-Tpy₂Ru) [81]. A 1:5 ratio of cationic monomer to the dicyclopentadiene afforded a membrane with 126% water uptake and OH^- conductivity of 28.6 mS/cm at 30 °C (IEC of 1.4 mmol/g) [81]. The membrane was stable in 1 M NaOH at room temperature over 6 months [81]. In a follow up study, the authors noted that cross-linked bis(terpyridine)Ru based polymers tended to have higher hydration numbers and lower bicarbonate conductivity than some

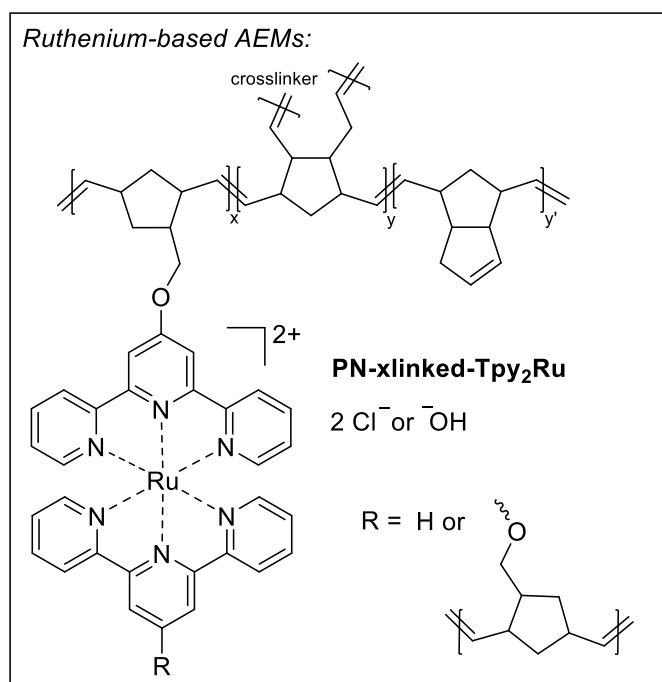


Fig. 15. Ruthenium-based polymers examined as AEMs.

comparable materials with smaller cations (e.g. benzyltrimethylammonium and 3-benzyl-1-methylimidazolium). It was hypothesized that the larger occupied volume of the $[\text{bis(terpyridine)Ru}]^{2+}$ led to these differences in hydration and conductivity [90].

A 2017 study by Kwasny and Tew explored how altering the site of crosslinking in the polymer backbone impacted water uptake in Ru-functionalized polynorbornenes [88]. In addition to preparing membranes with pendant heteroleptic ruthenium cations (derived from the monomer shown in Fig. 14), AEMs were also synthesized from homoleptic ruthenium complexes functionalized with polymerizable norbornene units on each of the terpyridine ligands for use as crosslinkers [88]. In each instance, ratios of crosslinking monomer to non-crosslinking monomer and ionic to insulating monomer were held constant at 1:5, and a substantially lower water uptake of 30–35% was obtained by utilizing a homoleptic ruthenium cation in comparison to the AEMs functionalized with the heteroleptic cation (water uptake up to ~230%) [88]. Interestingly, a significant reduction in the Cl^- conductivity is observed when implementing the homoleptic ruthenium complex (0.92 mS/cm at 80 °C) as opposed to the heteroleptic derivative (3.40 mS/cm at 80 °C) [88], suggesting that crosslink density plays an important role in the performance of these materials.

7. Nickel-based AEMs

Nickel-based cations have also been examined for use in anion-exchange membranes [88]. Similar to $[\text{bis(terpyridine)Ru(II)}]^{2+}$, the redox potential for $[\text{bis(terpyridine)Ni(II)}]^{2+}$ is outside of the operating window of a fuel cell [88]. To our knowledge there are no studies that discuss stability of this cation in alkaline media, which would provide key insight for their use in hydroxide transport membranes. In Kwasny and Tew's comparative study from 2017, a homoleptic $[\text{bis(terpyridine)Ni(II)}]^{2+}$ AEM was prepared using identical ratios of crosslinking monomer to non-crosslinking monomer and ionic to insulating monomer (1:5 in each case) as in the previously mentioned $[\text{bis(terpyridine)Ru(II)}]^{2+}$ and $[\text{bis(terpyridine)Co(II)}]^{2+}$ AEMs [88]. The nickel-functionalized derivative (Fig. 16 – PN-xlinked-Tpy₂Ni) outperformed the ruthenium and cobalt analogues, exhibiting a Cl^- conductivity of 2.4 mS/cm at 80 °C and 36% water uptake (IEC = 0.49 mmol/g) [88]. Tew and coworkers also synthesized $[\text{bis(terpyridine)Ni(II)}]^{2+}$ AEMs through RAFT polymerization and crosslinking via thiol-ene click reaction to promote formation of ion clusters with the expectation that this could improve transport (Fig. 16 – PS-xlinked-Tpy₂Ni) [91]. The water uptake for this material was quite high at 238%, with a Cl^- conductivity of 1.34 mS/cm at 80 °C (IEC = 1.13 mmol/g) [91]. It was possible to lower water uptake by reducing cation content in the membrane, however, lower IEC polymers were noted to be too brittle for conductivity testing [91].

8. Alkali metal AEMs

In the last five years, anion-exchange membranes utilizing the host-guest interaction between crown ethers and alkali metal cations have also attracted attention. Some researchers have utilized dual cation systems with both ammoniums (Tröger's base [92,93] or DABCO [94]) and crown ethers for ion transport. In these studies, the addition of the crown ether decreased water uptake, making higher ammonium content accessible, which in turn raised the hydroxide conductivity. In 2017, Zhu and coworkers established that crown ethers can work as the sole ion conductor in an AEM, synthesizing a crosslinked polyphosphazene (Fig. 17 – P=N-15-crown-5) with pendant crown ethers [95]. The P=N-15-crown-5 had a OH^- conductivity of 78.6 mS/cm at 90 °C and only 62.6% water uptake for a film with a reasonably high IEC (1.59 mmol/g) [95]. In addition, Wang and coworkers have synthesized AEMs by appending crown ether groups to polyvinyl alcohol [96,97] and chitosan [98] backbones (Fig. 17 – PVA-18-crown-6 and Chitosan-18-crown-6). The highest performing among these was a

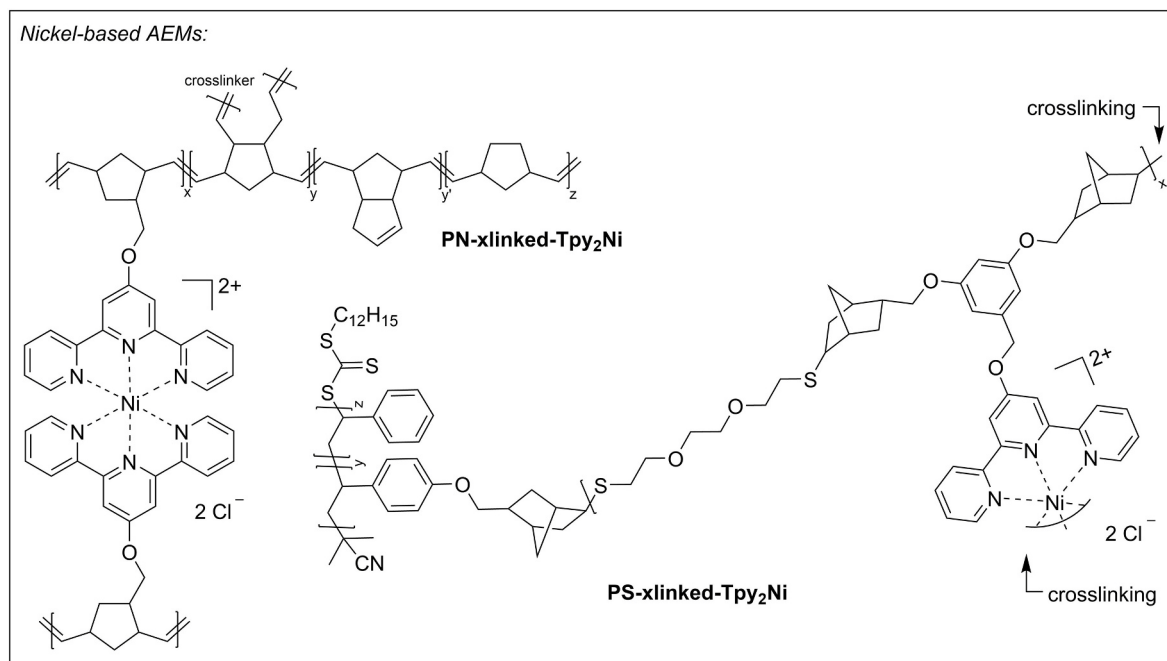


Fig. 16. Nickel-based polymers examined as AEMs.

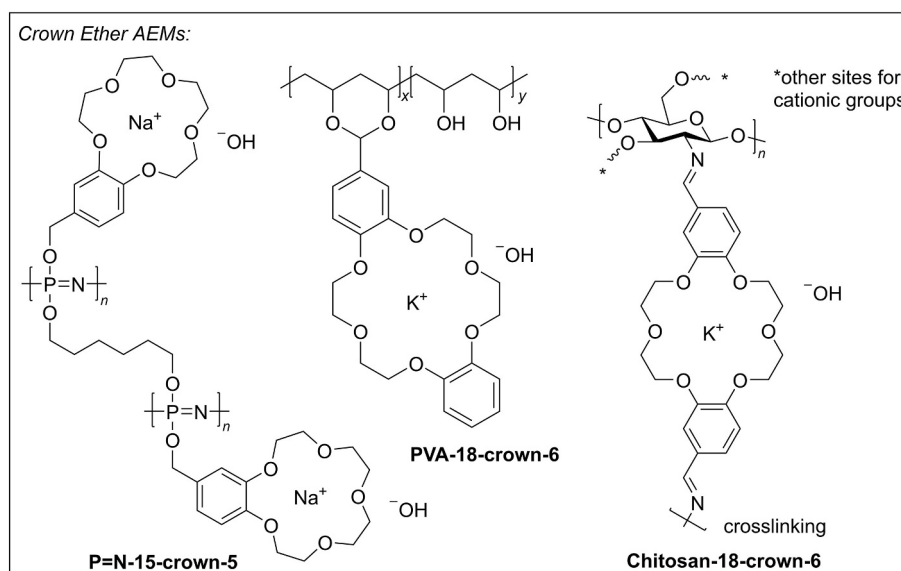


Fig. 17. Crown ether polymers examined as AEMs.

bis-crown ether AEM (Fig. 18) with OH^- conductivity reaching an exceptional 235 mS/cm at 80 °C and a water uptake of ~135% (IEC = 3.51 mmol/g) [97]. Alkaline stability has been examined by soaking these membranes in various concentrations of NaOH or KOH for 168–480 h [96–98]. Less than 10% of ionic conductivity was lost in each case, and the authors noted that the backbone seemed to be the major area for degradation as opposed to the crown ether side group [96–98].

9. Conclusions

In the design of anion-exchange membrane materials, the choice of cation, polymer backbone, and tethering chemistry are all critically important to alkaline stability. The reports discussed in this review highlight the unique potential of heavy main group and metal-based cations combined with organic polymers to make hybrid materials for

transport. To date, a great deal of work has focused on the alkaline stability of the inorganic moieties to ensure that the chosen derivatives are suitable for their targeted applications. Cations derived from heavier elements offer an incredible selection of substituents around the positively charged center, and several of the families discussed above have improved stability over ammonium cations when properly designed. As research in this area continues, we anticipate that further exploration of the vast reaches of inorganic chemistry will lead to novel AEM designs and further exciting advances. Below are some suggested opportunities for future directions in this area.

10. Opportunities and challenges

Membrane Stability. As much exciting work is still to come, one critical feature is standardization of alkaline stability measurements to

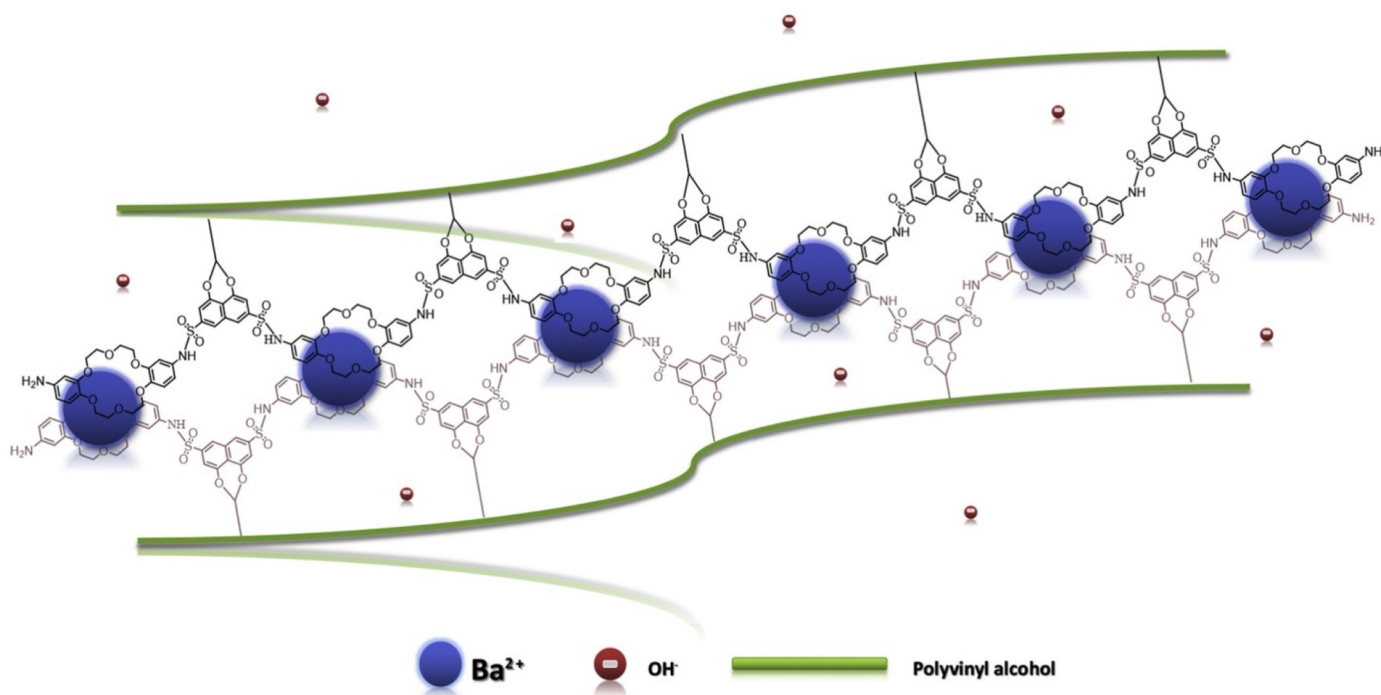


Fig. 18. Bis-crown ether appended to a poly(vinyl alcohol) backbone for hydroxide conduction. Reproduced with permission from Ref. [97].

ensure straightforward comparison of different materials. Building from recent reports [29,99], we recommend stability studies in 1 M KOH for 1000 h as well as in 5 M and 10 M KOH over 500 h. Pursuit of heteroatom-free polymer backbones should be a priority for improving long-term stability given the instability of poly(aryl ether sulfones) and poly(phenylene oxide) AEMs [30–32].

Cation Size. Most of the alkaline-stable inorganic cations which have been identified as candidates for AEMs have higher molecular weights and occupy larger volumes than quaternary ammoniums (particularly trimethylammoniums). Generally, this leads to lower effective concentrations of cation along the polymer chain (lower IEC), often with higher hydration numbers (increased swelling), and lower conductivities when compared to ammonium-based AEMs. As the field matures, strategies to improve on the performance of these materials is key to future progress. This can be accomplished in several ways, with control over morphology as a natural choice to improve transport. The example from Balsara and coworkers [51], where Br^- conductivity tripled by increasing the domain size in a diblock copolymer, stands as a particularly striking example of the differences in conductivity that can be achieved by controlling polymer organization. Arges, Nealey, and coworkers have also highlighted the importance of interconnected ionic domains in block copolymer AEMs [100,101]. Clearly, control over the polymer composition to tune morphology, phase separation, and domain connectivity will be key to future advances. In our own work on vinyl addition polynorbornenes, we noted higher water uptake in block copolymers than in the equivalent statistical copolymers [69]. This is particularly important when utilizing bulky cationic groups, and approaches to control water uptake (e.g. cross-linking) may also be vital design strategies for future work.

Physical Characterization and In-Situ Device Testing. Given that novel cationic side groups are certain to impact chain-entanglement molecular weight, film-forming properties, and thermal stability; in-depth examination of mechanical properties of novel hybrid polymers (stress-strain, strength, elongation at break) is important. An improved understanding of the differences which arise for specific polymer backbones upon moving from the more typical quaternary ammonium groups to the often more bulky inorganic frameworks would be sure to guide future AEM design. Further investigation of novel AEMs in electrochemical

cells would be beneficial [59,83,94,97], as this area of research remains in its infancy for the inorganic systems.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. It should be noted that K.J.T.N and J.G. have a submitted patent on some of their work on aminophosphonium norbornene polymers (Pat. Appln. No: 17/243,877).

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.polymer.2022.124811>.

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