



Phosphonium-Functionalized Polyethylene: A New Class of Base-Stable Alkaline Anion Exchange Membranes

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S Supporting Information

ABSTRACT: A tetrakis(dialkylamino)phosphonium cation was evaluated as a functional group for alkaline anion exchange membranes (AAEMs). The base stability of $[P(N(Me)Cy)_4]^+$ was directly compared to that of $[BnNMe_3]^+$ in 1 M NaOD/CD₃OD. The high base stability of $[P(N(Me)Cy)_4]^+$ relative to $[BnNMe_3]^+$ inspired the preparation of AAEM materials composed of phosphonium units attached to polyethylene. The AAEMs (hydroxide conductivity of $22 \pm 1 \text{ mS cm}^{-1}$ at 22 °C) were prepared using ring-opening metathesis polymerization, and their stabilities were evaluated in 15 M KOH at 22 °C and in 1 M KOH at 80 °C.

Fuel cell devices are currently being investigated for a variety of applications, as they efficiently convert the chemical energy stored in a fuel (e.g., H₂ or CH₃OH) directly into electrical energy.¹ One type of fuel cell that has been investigated extensively is the so-called proton exchange membrane fuel cell (PEMFC). PEMFCs operate at relatively low temperatures (50 to 100 °C) with high efficiencies and consist of an ionically conducting polymeric material pressed between the cathode and anode to provide ion conduction and electrical insulation. PEMFCs operating under acidic conditions commonly employ Nafion, a perfluorinated polymer with pendant sulfonic acid groups that facilitate the flow of protons.² Unfortunately, the oxygen reduction reaction is rate-limiting for acidic fuel cells, and the most commonly employed cathode materials are based on platinum and its alloys.¹ The high cost of platinum has led to investigations into fuel cells that operate under alkaline conditions, since less expensive metals, such as silver, can be used as the cathode catalyst.³ Consequently, researchers have attempted to prepare alkaline anion exchange membranes (AAEMs) with stability and conductivity similar to those of Nafion.⁴

Ideal AAEMs would be mechanically and chemically robust, exhibit good hydroxide ion conductivity, and display limited swelling. Various polymer backbones have been investigated to date, including hydrocarbon polymers prepared via ring-opening metathesis polymerization (ROMP),⁵ fluoropolymers,⁶ polysulfones,⁷ polyarylenes,⁸ and poly(ether-imide)s.⁹ These polymeric supports contain pendant ammonium cations to facilitate hydroxide ion conduction from the cathode to the anode. However, the degradation pathways for ammonium cations under alkaline conditions have been well-documented,¹⁰ and the long-term stability of the ammonium cation under fuel

cell operating conditions remains a concern.¹¹ This has sparked investigations of other cationic species appended to polymeric supports for use in alkaline membrane fuel cells (AMFCs), including guanidinium¹² and imidazolium¹³ cations. Holdcroft and co-workers recently reported a sterically crowded benzimidazolium polymer that exhibits excellent base stability when heated to 60 °C in 2 M KOH over a 13 day period.¹⁴ Tetraalkylphosphonium cations represent another exciting class of functional groups for AAEMs, as the synthesis of phosphonium ionomers has already been established.¹⁵ Both the benzyltrimethylphosphonium ($[BnPMe_3]^+$)¹⁶ and benzyltris-(2,4,6-trimethoxyphenyl)phosphonium¹⁷ cations are being evaluated in AAEM materials. While the tetraalkylphosphonium cation ($[PR_4]^+$) is attracting attention in AAEMs, the tetrakis(dialkylamino)phosphonium cation ($[P(NR_2)_4]^+$) is also of interest.^{18,19} Recent reports have shown the exceptional stability of $[P(NR_2)_4]OR'$ compounds ($R' = H, \text{alkyl}$), and their applications in phase transfer,¹⁹ transesterification,²⁰ and polymerization²¹ reactions have been demonstrated. Herein we report a new class of hydroxide ion exchange membranes that consist of a tetrakis(dialkylamino)phosphonium cation appended to polyethylene. These materials exhibit excellent stability in strongly basic solution.

The $[BnNMe_3]^+$ cation has been commonly employed in AAEMs. As a result, we chose to compare its base stability to that of the bulky $[P(N(Me)Cy)_4]^+$ cation. Since $[BnNMe_3]OH$ exhibits negligible degradation over 29 days in 1 M NaOH in water at 80 °C,^{10f} the stability in methanol was explored because this solvent (1) accelerates cation degradation, (2) often dissolves polyatomic cations better than water, and (3) is applicable to direct methanol fuel cells (DMFCs).²²

In a sealed fluoropolymer-lined vessel, $[BnNMe_3]Br$ (0.1 M) and NaOD (1 M) were combined in CD₃OD at 80 °C. This resulted in 66% degradation of the $BnNMe_3$ cation after 20 days (Figure 1).²² In solution, $[BnNMe_3]^+$ seems to degrade primarily by nucleophilic attack at either the benzylic or methyl positions (as confirmed by ¹H NMR and GC–MS analyses). Deuterium scrambling was also observed at the benzylic and N-methyl positions in the degradation products, suggesting reversible formation of a nitrogen ylide species in solution. In stark contrast, when $[P(N(Me)Cy)_4]BF_4$ (0.1 M) and NaOD (1 M) were dissolved in CD₃OD, no degradation of $[P(N(Me)Cy)_4]^+$ was observed over a 20 day period at 80 °C (as measured by ¹H and ³¹P NMR spectroscopy). This

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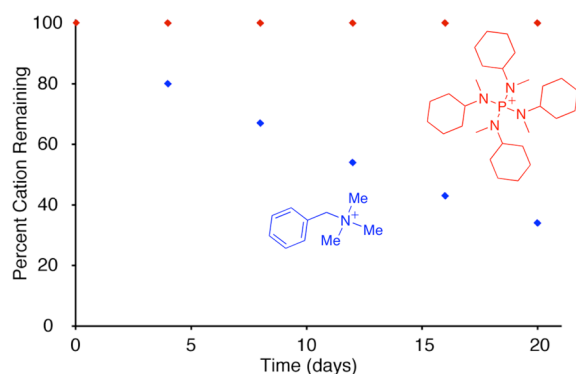


Figure 1. Stability of $[\text{BnNMe}_3]^+$ and $[\text{P}(\text{N}(\text{Me})\text{Cy})_4]^+$ in 1 M NaOD/ CD_3OD at 80 °C.

stability under basic conditions in methanol is noteworthy and suggests that the tetrakis(dialkylamino)phosphonium cation may be a promising functional group choice for AAEM fuel cells, especially DMFCs.

To investigate further the stability of the tetrakis-(dialkylamino)phosphonium cation, we sought to synthesize and characterize a discrete alkoxide species. $[\text{P}(\text{N}(\text{Me})\text{Cy})_4]\text{BF}_4$ was combined with KOH in methanol; precipitation and filtration of KBF_4 followed by removal of the solvent afforded crystals suitable for X-ray diffraction. The solid-state molecular structure of $[\text{P}(\text{N}(\text{Me})\text{Cy})_4][\text{OMe}]\cdot 3\text{MeOH}$ (**1**) is displayed in Figure 2. Our ability to obtain this crystal structure further

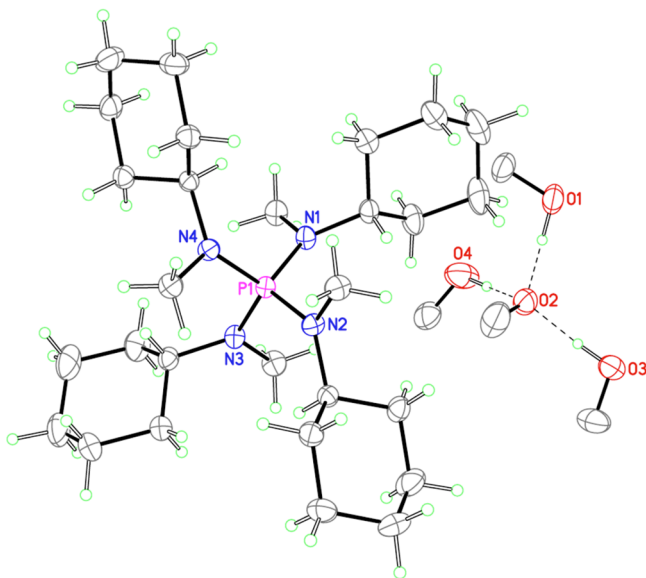


Figure 2. Molecular structure of **1**, with thermal ellipsoids set at 40% probability.

documents the unique stability of the phosphonium cation, since very few other organic cations are known to be stable enough to crystallize with a methoxide anion. Two other reports describe salts of organic cations with methoxide. Love and co-workers reported a tetraprotonated polypyrrole macrocycle crystallized with three tosylate counterions and one methoxide counterion,²³ and Ou and co-workers described an ion pair in which a hydrogen bond exists between an NH_3 moiety and the anionic methoxide.²⁴

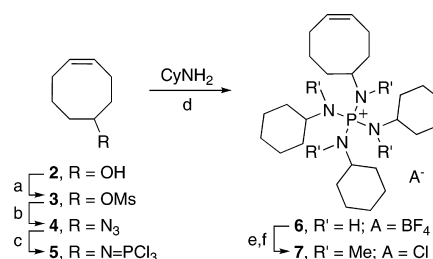
The P–N bond lengths in **1** [1.639(1)–1.655(1) Å] are quite similar to those reported for $[\text{P}(\text{N}(\text{Me})\text{Cy})_4]\text{PF}_6$

[1.636(1) Å].¹⁹ The anionic methoxide is hydrogen-bonded to three methanol molecules.²⁵ The short O–O separations between the neighboring methanol molecules and the methoxide anion of **1** (2.576–2.636 Å) suggest relatively strong hydrogen bonding; a typical O–O distance for a hydrogen-bonded system is 2.75 Å. These strong O–H contacts provide significant energetic stabilization to the reactive methoxide anion.²⁶

The stability of $[\text{P}(\text{N}(\text{Me})\text{Cy})_4]\text{BF}_4$ in 1 M NaOD/ CD_3OD and the preparation of crystalline **1** suggested that these delocalized phosphonium cations might be suitable for AAEM applications. Although there have been previous reports describing polymers with appended dialkylaminophosphoniums,^{18,27} none have been examined under fuel-cell-relevant conditions. This prompted us to target a polyethylene-based phosphonium ionomer.

Our group has previously reported two separate cross-linked polymer networks bearing pendant ammonium groups as potential AAEMs.^{5c,d} The ammonium groups were appended to norbornyl and cyclooctenyl derivatives, and the functionalized monomers were polymerized via ROMP. The commercially available Grubbs second-generation catalyst (Ru-cat) was employed since it is tolerant of quaternary ammonium halides.^{5,28} The synthesis of non-cross-linked AAEMs has also been achieved using ROMP.^{5b} A cyclooctenyltrimethylammonium monomer was copolymerized with cyclooctene in the presence of Ru-cat to afford an unsaturated copolymer. Hydrogenation of this material yielded a solution-processable and mechanically strong ammonium-functionalized polyethylene [hydroxide conductivity at 50 °C ($\text{OH}^- \sigma_{50}$) = 65 mS cm^{-1}]. Using a similar strategy, a tetrakis(dialkylamino)-phosphonium-functionalized cyclooctene was targeted and prepared in six steps from 5-hydroxy-1-cyclooctene (**2**) (Scheme 1).²⁹ Mesylation of **2** followed by reaction with

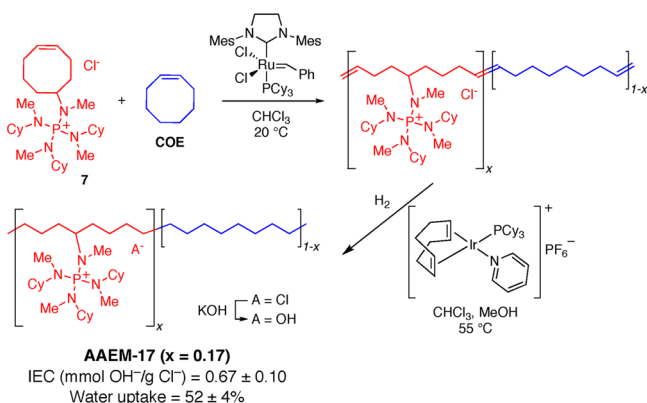
Scheme 1. Phosphonium Monomer Synthesis^a



^aReagents and conditions: (a) 1.2 equiv of MsCl , pyridine, 0 °C; (b) 1.5 equiv of NaN_3 , DMSO, 50 °C; (c) 5 equiv of PCl_3 , toluene, 70 °C; (d) CH_2Cl_2 , 0 °C, followed by workup with 1 M NaBF_4 ; (e) 5 equiv of Me_2SO_4 , 40 equiv of NaOH , H_2O , chlorobenzene, 70 °C; (f) chloride anion exchange resin.

NaN_3 afforded 5-azido-1-cyclooctene (**4**). A Staudinger reaction yielded iminophosphorane **5**, whose immediate reaction with cyclohexylamine produced phosphonium salt **6**. Methylation conducted using standard phase-transfer protocols yielded the tetrakis(dialkylamino)phosphonium cation (**7**) (Scheme 1). Monomer **7** was copolymerized with cyclooctene (COE) in the presence of Ru-cat in chloroform for 18 h (Scheme 2). ^1H NMR spectroscopy of the reaction mixture indicated that COE was incorporated into the growing polymer chain more readily than **7**. Thus, this polymerization strategy could potentially be modified to yield block copolymer

Scheme 2. Synthesis of Phosphonium-Functionalized Polyethylene



architectures, an area currently drawing interest with respect to AAEMs.^{7a,30} We are currently investigating the synthesis of random and block copolymers bearing these phosphonium moieties.

The unsaturated ROMP polymer was hydrogenated ($[(\text{COD})\text{Ir}(\text{py})(\text{PCy}_3)]\text{PF}_6$, $\text{CHCl}_3/\text{MeOH}$, 600 psig H_2 , 17 h), and ^1H NMR spectroscopy revealed nearly quantitative hydrogenation. The reduced copolymers (chloride form) were dissolved in a 1,2-dichloroethane/ethanol cosolvent mixture (1:1) and cast onto a glass dish preheated to 45°C , from which the volatiles were slowly evaporated to yield a film. The polymers were converted into their hydroxide form by soaking them in 1 M KOH for 2 h and washing with deionized water for 1 h. Samples containing a range of comonomer ratios were tested, but polymers with higher percentages of 7 exhibited excessive swelling at higher temperatures. The optimized AAEM used for conductivity and base-stability studies, AAEM-17, contained 17 mol % 7. Conductivity, ion exchange capacity and water uptake data for AAEM-17 are presented in Scheme 2.³¹ We suspect that the size of the tetrakis(dialkylamino)phosphonium cation inhibits packing of the polymer chains, resulting in a material with a high water uptake in view of the relatively low ion exchange capacity.

To investigate the stability of the phosphonium-functionalized membrane materials under highly alkaline conditions, we exposed AAEM-17 ($\text{OH}^- \sigma_{22} = 22 \pm 1 \text{ mS cm}^{-1}$) to a solution of 15 M KOH in water. The chloride form of the hydrogenated copolymer was immersed in 1 M KOH(aq) following the standard exchange procedure³¹ to obtain AAEM-17, which was immediately exposed to 15 M KOH(aq) at 22°C . Over a 138 day period, AAEM-17 was periodically removed from the 15 M solution and soaked in deionized water for 18 h to ensure complete rehydration. The membrane was re-exchanged with 1 M KOH(aq) and washed with water to remove any residual base, and the in-plane hydroxide conductivity was measured at 22°C . The data obtained are presented in Figure 3. Interestingly, no significant loss of conductivity was observed for AAEM-17 after exposure to 15 M KOH(aq) over the 20 week period. To investigate the stability of the membrane at elevated temperatures, AAEM-17 was exposed to 1 M KOH(aq) at 80°C . A small initial loss of conductivity (from 22 to 18 mS cm^{-1}) was observed after 3 days, but no further loss in conductivity was evident up to 22 days. The alkaline stability of the phosphonium-functionalized AAEM in 1 M KOH(aq) at 80°C suggests that these may be excellent candidates for higher-temperature AMFC devices.

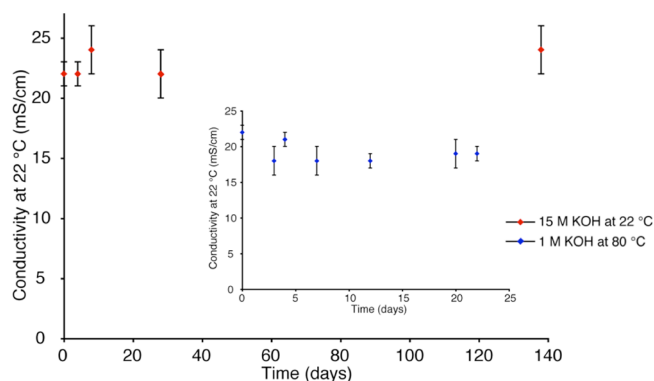


Figure 3. AAEM-17 hydroxide conductivity as a function of time after immersion in 15 M KOH(aq) at 22°C . Inset: AAEM-17 hydroxide conductivity as a function of time after immersion in 1 M KOH(aq) at 80°C .

In conclusion, the alkaline stability of a tetrakis(dialkylamino)phosphonium cation was evaluated and directly compared with that of benzyltrimethylammonium cation. In model compound investigations, the $[\text{P}(\text{N}(\text{Me})\text{Cy})_4]^+$ outperformed $[\text{BnNMe}_3]^+$. Consequently, a new methodology for appending these delocalized phosphonium cations to polyethylene was developed. The membrane stability of AAEM-17 in 15 M KOH at 22°C and 1 M KOH at 80°C confirmed that tetrakis(dialkylamino)phosphonium materials are promising candidates for testing in AMFCs. Our future work will focus on controlling the polymer morphology in an effort to increase the conductivity of these materials while retaining their excellent mechanical properties.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures and characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>. Crystallographic data are also available from the Cambridge Crystallographic Data Centre (<http://www.ccdc.cam.ac.uk/>) under deposition number CCDC 889152.

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Notes

The authors declare no competing financial interest.

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