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A Highly Conductive and Mechanically Robust OH⁻ Conducting Membrane for Alkaline Water Electrolysis

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Abstract

In an alkaline water electrolysis cell, a membrane is needed between the cathode and the anode to avoid mixing of hydrogen and oxygen products while enabling OH$^-\$ transport. Hydroxide ion conductivity and membrane mechanical properties are both important parameters that determine material constraints on low electrical resistance of a membrane versus sufficient structural integrity. Herein, we demonstrate a strategy to make membranes with both high OH$^-$ conductivity and mechanical strength. A chemically tailored OH$^-$ conducting polymer (qPPO) was synthesized via amination and subsequent quaternization of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and was blended with poly(vinyl alcohol) (PVA) to provide an environment analogous to basic water solutions. The –OH groups in PVA provide high-density Grotthuss mechanism conduction sites similar to water, which may be the key reason for the observed high OH$^-$ conductivity of the membranes. The PVA backbone was crosslinked to form a semi-interpenetrating network (semi-IPN) of PVA and qPPO; the resulting material contains PVA chemical crosslinks and hydrogen bonds between PVA and qPPO and between PVA with itself, all of which are believed to contribute to a high tensile strength. By tuning the PVA/qPPO ratio, the transport and mechanical properties were optimized. The membrane with 30% qPPO possesses both extraordinary conductivity (151 mS/cm at room temperature) - about 2.7 times as high as Nafion 117 in acidic conditions - and high ultimate tensile strength (126 MPa (dry), 41 MPa (wet)). This highly conductive polymer membrane also exhibits stability in alkaline water electrolysis at room temperature, a property that makes qPPO an interesting and potentially translational material for the design of hydroxide based electrochemical cells.

Introduction

Hydrogen is a clean fuel and a critical ingredient in the chemical industry (needed for hydrocracking of heavy petroleum fractions, production of ammonia, etc.). Currently, hydrogen is mainly produced by steam reforming from fossil fuels, which is counterproductive to the fight to lower CO$_2$ emissions.$^1$ Water electrolysis enables hydrogen production from renewable energy sources, such as solar, wind, and hydropower.$^2$
A membrane between the anode and cathode is required to separate the evolving hydrogen and oxygen gases while allowing ions to pass through.\textsuperscript{3,4} Water electrolysis performed at high pH has unique advantages over other pH conditions. Under acidic conditions, electrolysis using Nafion proton exchange membranes is effective but requires the use of costly precious metal catalysts to resist the corrosive environment;\textsuperscript{5,6} whereas for (near) neutral conditions, there are large energy losses from the pH gradient between the anode and cathode.\textsuperscript{7} In contrast, under basic conditions, non-precious Ni-based catalysts have satisfying activity and stability, which can make widespread H\textsubscript{2} production via electrolysis possible.\textsuperscript{4,5} Alkaline water electrolysis can run with a polymer electrolyte membrane and supporting electrolyte,\textsuperscript{8,9} or more recently, with the membrane and pure water only\textsuperscript{10-13}. Currently, there is an increasing interest in developing a robust OH\textsuperscript{-} conducting membrane analogous to Nafion, which is chemically stable, mechanically strong, a good gas separator, and a good proton conductor, for alkaline water electrolysis and fuel cells.\textsuperscript{14}

In addition to separating the product gases, the main objective of OH\textsuperscript{-} conducting membrane development is to design systems that minimize energy loss.\textsuperscript{15} In terms of membrane material properties, this objective can be achieved by creating a highly conducting membrane and making the membrane sufficiently thin to achieve the lowest possible resistance, while still maintaining desired gas barrier properties and a material system that is mechanically strong enough to remain intact during operation conditions. These goals yield implications for a number of material properties, including the maximizing of both OH\textsuperscript{-} conductivity and tensile strength, because with higher strength, the membrane can be made thinner, and energy loss can be minimized. Unfortunately, high conductivity and high ultimate tensile strength can be difficult to achieve simultaneously using common strategies. Conductivity is usually increased by increasing the ion-exchange capacity (IEC), which in turn increases water uptake to facilitate Grotthuss conduction, which is important for OH\textsuperscript{-} transport\textsuperscript{16}. On the other hand, excessive swelling of the membrane in water lowers its ultimate tensile strength.\textsuperscript{17,18} Ultimate tensile strength is usually increased by either crosslinking the ion conducting polymers\textsuperscript{19,20} or by the addition of reinforcing materials\textsuperscript{21}, such as poly(tetrafluoroethylene) (PTFE). Crosslinking lowers the flexibility of the polymer chains, while the use of reinforcing materials adds mass that contributes nothing to ion conduction; therefore, both approaches would lower the conductivity.
OH⁻ conductivity is proportional to the mobility of OH⁻ in the media. The mobility of OH⁻ in water (e.g. KOH aqueous solution) is very high ($2.064 \times 10^{-7}$ m$^2$ s$^{-1}$ V$^{-1}$ at infinite dilution at 298.15 K); it is lower than that of H⁺ but much higher than that of other ions.\textsuperscript{14} However, the effective mobilities of OH⁻ in polymer membranes are usually much lower than the value in aqueous solution.\textsuperscript{14} Recently, phase segregation strategies have been successfully employed to enhance the OH⁻ conductivity by increasing the OH⁻ mobility rather than increasing the IEC, in order to avoid excessive swelling in water.\textsuperscript{22-24} For example, an ABA triblock copolymer with one block of poly(arylene ether sulfone)s and two blocks of quaternary ammonium functionalized poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) has a OH⁻ conductivity of 93.1 mS/cm at 60 °C and a tensile strength of 24.2 MPa under fully humidified conditions at room temperature.\textsuperscript{23}

Hybrid membranes composed of a quaternized PPO and PVA have been studied for acid recovery application.\textsuperscript{25} They have high acid (H⁺) dialysis coefficients partly because the –OH groups can facilitate the transport of H⁺. We believe that –OH groups can also facilitate the transport of OH⁻ via Grothuss mechanism. However, micropores were formed in these membranes due to insufficient compatibility between the two polymers, which would be undesirable for the water electrolysis and bipolar membrane application as the pores could lead to gas crossover and low anion perm-selectivity. Thus, a new polycation with higher compatibility with PVA should be designed and synthesized.

Herein, a new anion exchange polymer is co-solubilized with PVA to form a blended network, rich with alcohol groups, which resembles the case of KOH aqueous solution. The OH⁻ conducting polymer (qPPO) we designed is miscible with PVA over a broad range of concentrations and is aqueous solution processible. It is a polycation with an aromatic PPO backbone. It has quaternary ammonium cation groups that act as hopping sites for OH⁻ ion and enable anion perm-selectivity, and tertiary amine groups that form hydrogen bonds with PVA and provide pH-dependent solubility in water. Poly(vinyl alcohol) (PVA) was blended with qPPO and crosslinked to form a semi-interpenetrating network, with the intent that PVA play a role similar to water. The resulting polymer network, which is dense with alcohol functionality and positively charged sites, is designed to solvate the OH⁻ conducting polymer and facilitate the Grothuss mechanism for ion conduction, thus enhancing the mobility of OH⁻. At the same time, unlike liquid water that diminishes tensile strength, PVA can actually enhance tensile strength due to the
hydrogen bonds and crosslinks it presents in the network. Moreover, the qPPO structure was designed to exhibit limited degradation pathways, with large steric hindrance built around vulnerable sites for hydroxide ion attack. The overall performance of the membranes can be optimized by tuning the amount of qPPO relative to PVA.

**Experimental Section**

2.1 Materials

Chemicals were all purchased from Sigma Aldrich except for trimethyloxonium tetrafluoroborate and deuterated solvents, which were purchased from Alfa Aesar and Cambridge Isotope Laboratories respectively. PPO had an M\textsubscript{w} of 30,000 and an M\textsubscript{n} of 20,000. The Sn was in powder form with a particle size of < 0.045 mm. The 1,2-dichloroethane was dried over 3 Å molecular sieves for more than a week before being used in the synthesis of PPO-NMe\textsubscript{3}\textsuperscript{+}BF\textsubscript{4}\textsuperscript{-}. The PVA has an M\textsubscript{w} of 146,000-186,000 and was 99+% hydrolyzed. The Nafion 117 membranes were purchased from Sigma-Aldrich, and Neosepta AHA anion-exchange membrane (AEM) from Ameridia. All water used was deionized.

2.2 Synthesis of qPPO

2.2.1 Synthesis of PPO-NO\textsubscript{2}

5 g PPO was dissolved in 100 mL 1,2-dichloroethane at 30 °C. 12 mL 70% HNO\textsubscript{3} and 4 mL 95%-98% H\textsubscript{2}SO\textsubscript{4} were mixed after both being cooled down to −20 °C. The acid mixture was poured into the PPO solution. The reaction mixture turned red immediately. It was stirred at 30 °C for 4 hours. The reaction was quenched by adding 100 g of ice, and the mixture was poured into 600 mL methanol to precipitate PPO-NO\textsubscript{2}. The product was filtered and rinsed with methanol four times. Then, it was dried under vacuum at room temperature for 24 h to yield 6.39 g PPO-NO\textsubscript{2} (93% yield).

2.2.2 Synthesis of PPO-NH\textsubscript{2}

6.39 g (38.7 mmol of repeat units) PPO-NO\textsubscript{2}, 27.57 g (232.2 mmol) Sn powder, 406 mL methanol, and 406 mL 37% HCl (~4.88 mol) were added to a flask in this order. The addition of methanol was made to better disperse the highly hydrophobic PPO-NO\textsubscript{2}. The flask was connected
to a condenser and the mixture was stirred at 60 °C under N₂ protection for 48 hours. The reaction product PPO-NH₃⁺Cl⁻ aggregated into a single chunk. The liquid solution was quickly decanted and the chunk was subsequently rinsed by 37% HCl three times, dissolved in 150 mL methanol, and filtered. 15 mL 5 M NH₃ aqueous solution was added to the filtered methanol solution to deprotonate PPO-NH₃⁺Cl⁻ so that PPO-NH₂ was precipitated. PPO-NH₂ was separated by centrifugation and rinsed with methanol four times. The product was dried under vacuum for 24 h, and stored in a glove box (unstable in air). 4.71 g (90% yield) of PPO-NH₂ was obtained. The structure and purity were confirmed by H-1 and C-13 NMR (Figure S1), and the degree of amination was found to be 100% (of all the repeat units) from the H-1 NMR spectrum.

2.2.3 Synthesis of PPO-NMe₂

In a glove box, 4.71 g (34.8 mmol of repeat units) PPO-NH₂ was dissolved/dispersed in 150 mL N,N-dimethylformamide. 12.35 g (87.0 mmol) CH₃I was added and the mixture was stirred at room temperature for 12 h. The polymer solid gradually fully dissolved during the reaction. 9.32 g (87.0 mmol) 2,6-lutidine (a hindered base) was then added to the reaction mixture. The polymer precipitated immediately due to deprotonation. The reaction mixture was stirred at room temperature for another 36 h and taken out of the glove box. 50 mL 1 M NH₃ aqueous solution was added. The insoluble polymer was filtered and rinsed with water four times. The product was dried under vacuum at 70 °C for 24 h and then quickly transferred to and stored in a glove box. 5.15 g PPO-NMe₂ (91% yield) was obtained. The structure and purity were confirmed by H-1 and C-13 NMR (Figure S2).

2.2.4 Quaternization of PPO-NMe₂

In a glove box, 5.15 g (31.6 mmol of repeat units) PPO-NMe₂ was dissolved in 150 mL anhydrous 1,2-dichloroethane. 9.38 g (63.2 mmol) trimethyloxonium tetrafluoroborate fine powder (ground using a mortar and pestle) was added to the solution. The reaction mixture was stirred at 1500 rpm at room temperature for 48 h and then taken out of the glove box. The reaction was quenched by adding 10 mL of methanol. The solvent (1,2-dichloroethane and methanol) was removed by rotovap. The remaining solid was dissolved in 150 mL 0.02 M HBF₄ aqueous solution, and the insoluble impurities were filtered and removed. Precipitation of the polymer product was done by pouring the aqueous solution into 850 mL methanol. The solid was separated by centrifugation (up to 10 h). The qPPO product was redissolved in HBF₄ and reprecipitated in
methanol for further purification and was dried in a 50 °C oven for 48 h. 7.68 g qPPO in HBF₄ form was obtained. The structure and purity of the product were confirmed by its proton NMR spectrum (Figure S3), and the degree of quaternization was found to be 70% from the same spectrum. The yield was then calculated to be 93%.

2.3 qPPO-PVA semi-interpenetrating network (semi-IPN) membrane preparation

qPPO was dissolved in 0.02 M HBF₄ to form a 1 wt% solution. 1 g PVA was dissolved in 90 g water by stirring at 90 °C for 12 h. After the PVA solution was cooled to room temperature, it was diluted to 1 wt% by adding water. To fabricate membranes with different compositions with respect to qPPO and PVA (0%, 10%, 20%, ..., 100% qPPO), x mL qPPO solution, (10 - x) mL PVA solution, and 0.50 mL of 0.1 wt% glutaraldehyde aqueous solution were mixed (x = 0, 1, 2, ..., 9, 10). The mixtures were drop cast on PTFE boards and allowed to dry under ambient conditions for two days. Then, 5 M NH₃ aqueous solution was poured on the dry membranes to deprotonate the –NHMe₂⁺ groups in qPPO. After sitting for 3 h with the solution, the membranes were rinsed with deionized water, then dried at 80 °C for 12 h. The thicknesses of the membranes obtained were about 20 µm.

2.4 Nuclear magnetic resonance (NMR)

Spectra were obtained on a 300 MHz Varian Mercury 300 NMR Spectrometer (Software: VNMR 6.1c) or a 400 MHz Bruker Avance-400 NMR Spectrometer (Software: TopSpin 3.1). The solvent for PPO-NH₂, PPO-NMe₂, and qPPO (HBF₄ form) were N,N-dimethylformamide-d₇, tetrahydrofuran-d₈, and D₂O, respectively.

2.5 Fourier-transform infrared (FTIR) spectroscopy

The FTIR spectrum of a freestanding dry qPPO-PVA membrane was recorded using a JASCO FT/IR-4100 spectrometer under continuous N₂ purge. Acquisitions were done with 1024 scans.

2.6 Atomic force microscopy (AFM)

AFM images were taken in tapping mode using a Multimode AFM (Veeco Metrology). An antimony (n) doped Si cantilever with a force constant of 40 N/m (Bruker RTESPA-300) was used to image the samples under ambient conditions.
2.7 Ion-exchange capacity (IEC) determination by back-titration

The dry membranes in BF$_4^-$ form were weighed ($m$) and then soaked for 48 h in an excess amount of 1 M NaOH (replaced by new solutions three times meanwhile). They were rinsed with deionized water and then immediately immersed in 50 mL 0.05 M HCl standard for 24 h. The solutions were titrated with a standardized 0.05 M NaOH solution. Control HCl solutions with no membranes were also titrated with NaOH. The NaOH volume difference between the titration of the control and the sample was used to calculate the amount of OH$^-$ in the membrane in mmol, which was divided by $m$ to get the IEC number.

2.8 Water uptake

The membranes (counterion BF$_4^-$) were soaked in deionized water for 48 h at room temperature to get fully hydrated. They were taken out and weighed ($W_w$) immediately after the excess water on the surface was wiped with tissue paper. The wet membranes were dried in a vacuum oven at 80 °C for 48 h, and the dry weights ($W_d$) were measured. The water uptake ($W_u$) was calculated using the formula below:

$$W_u = \frac{W_w - W_d}{W_d} \times 100\%.$$

The water uptakes were not reported for membranes in OH$^-$ form because qPPO was found decomposed under the drying conditions, while it was stable with the relatively non-nucleophilic counterion BF$_4^-$. This issue was also dealt with by other researchers in a similar way.\textsuperscript{27}

2.9 Through-plane conductivity measurement

An H-cell (Figure S4, Glass Shop, Department of Chemistry, University of Manitoba) composed of two symmetrical chambers, each with a main open compartment for a working electrode and a Luggin capillary for a reference electrode, was clamped around each membrane after measuring its thickness in the dry state using a micrometer. Pt wires (2.0 mm diameter, 99.9%, Sigma-Aldrich) were used as working electrodes, while saturated calomel electrodes (CH Instruments) were used as reference electrodes in the Luggin capillaries that were pointed to the membrane (four-electrode configuration). Both chambers were filled with 6 M KOH. The setup sat for 1 h and then a current of 0.005 A was applied for 30 min to equilibrate the membrane and solution phases, followed by exchanging for fresh 6 M KOH solution. An increasing current was
applied by an electrochemical workstation (Princeton Applied Research) through the two working electrodes performing water electrolysis. The voltage drop across the membrane was determined by measuring the voltage difference of the two reference electrodes using a Keithley 2110-120 5.5-Digit Dual-Display Multimeter. The resulting apparent membrane resistance $R_{ap}$ was calculated by linear fitting the current-voltage curve. A control measurement without a membrane was conducted to determine resistance $R_{cell}$, which was subtracted from the apparent membrane resistance. The conductivity $\sigma$ was calculated using:

$$\sigma = \frac{t}{(R_{ap} - R_{cell})A}$$

where $t$ is the membrane thickness and $A$ is the membrane area exposed to solution. Besides the membranes developed by us, Neosepta AHA anion-exchange membranes were measured under the same conditions. For comparison, the proton conductivity of a Nafion 117 membrane (Sigma-Aldrich, used as received) was measured in the same way, except using 30 wt% $\text{H}_2\text{SO}_4$ as the electrolyte. All the conductivity results above were averaged over three samples. The error reported is the standard deviation. All the conductivity measurements above were conducted at room temperature. The conductivity was also measured at different temperatures for the 30% qPPO membrane using the same method. To control the temperature, the H-cell was placed in an ESPEC SH-241 Bench-top Type Temperature & Humidity Chamber. The temperature was increased from 10 °C to 50 °C in increments of 5 °C. After each 5 °C increase, we waited for 35 min before starting the measurement.

The OH⁻ conduction of the membrane with 30% qPPO was also tested at current density ($j$) from 0 to a high value of 1.0 A/cm². The experiment was performed with 6 M KOH and the same H-cell apparatus. The electrochemical workstation was replaced by Gw Instek PSP-405 Programmable Power Supply as the power source. The electric field across the membrane ($E$) was calculated by

$$E(j) = \frac{V(j) - V_{control}(j)}{t},$$

where $t$ is the membrane thickness in the dry state, $V$ and $V_{control}$ are the voltage difference between the two reference electrodes with and without the membrane, respectively.

2.10 Perm-selectivity
The setup of this experiment is the same as the one used in conductivity measurements except without working electrodes and the electrochemical workstation, as conducted by others. The two chambers were initially both filled with 0.02 M KOH, and the voltage difference between the two reference electrodes $\phi_0$ was measured for control. The two chambers were then exchanged for 0.02 M KOH on one side and 0.10 M KOH on the other side. The solutions were stirred and were constantly replaced by new solutions by pipetting to keep their concentrations at 0.02 M and 0.10 M. The voltage difference between the two reference electrodes $\phi$ was closely monitored and was recorded once stable. The total ionic concentration $\Gamma = \sum c_i z_i^2$ ($c_i$ is the molar concentration of ion i, $z_i$ is the charge number of that ion) is 0.04 M for the 0.02 M KOH solution, and 0.20 M for the 0.10 M solution. The activity coefficients of OH$^-\ Y$ in water are 0.900 at $\Gamma = 0.02$ M, 0.855 at $\Gamma = 0.05$ M, and 0.76 at $\Gamma = 0.20$ M, while the value at $\Gamma = 0.04$ M is not available. Assuming linearity, the activity coefficient of OH$^-$ at $\Gamma = 0.04$ M is estimated to be 0.870. Therefore, for an ideally OH$^-$ perm-selective membrane, the voltage is

$$\phi_{\text{ideal}} = \frac{RT}{F} \ln \frac{c_2 Y_2}{c_1 Y_1} = 37.9 \text{ mV}.$$  

The (apparent) perm-selectivity is reported as $(\phi - \phi_0)/\phi_{\text{ideal}}$ (averaged over three samples; the error reported is the standard deviation).

2.11 Mechanical characterization

The qPPO-PVA membranes and Neosepta AHA AEMs were cut into strips approximately 35 mm × 8 mm and 35 mm × 3 mm respectively. The stress-strain curves were measured by TA Instruments Q800 Dynamic mechanical analyzer in “DMA controlled force” mode at 25 °C and a stress ramp rate of 5 MPa/min, from which the values of ultimate tensile strengths and elongations-at-break were extracted (averaged over three samples; the error reported is the standard deviation). The preload stress was 5 kPa. The membranes were tested both in the dry state and the wet state. They were made dry by keeping in a vacuum desiccator over P$_2$O$_5$ for more than 3 days. They were made wet by soaking in deionized water for 48 h. The qPPO-PVA membranes tested were with BF$_4^-$ counterion, and the Neosepta AHA AEMs were used without ion exchange.

2.12 qPPO chemical stability test
A piece of qPPO was immersed in 6 M KOH at room temperature ((22 ± 1) ℃) for 10 days. Then, it was filtered out, rinsed with 6 M NaOD in D₂O once, and dissolved in DCl/D₂O for proton NMR characterization.

Results and Discussion

3.1 Synthesis of qPPO

The structural design of the OH⁻ conducting polymer is based on four considerations. First, the backbone polymer is synthetically easy to functionalize. Second, it is important that the OH⁻ conducting polymer be miscible with PVA. However, it is uncommon for two polymers to be miscible with each other since the entropy gain from mixing is small. An enthalpic driving force from secondary interactions such as hydrogen bonds is needed for a polymer blend to be thermodynamically favorable. Therefore, the OH⁻ conducting polymer is designed to have sites for hydrogen bond formation with PVA. Third, aqueous solution processibility is desired as it ensures the fabrication cost is low and the processing is simple. Since the ion conducting polymer should not undergo dissolution under basic conditions, it should be soluble at a lower pH to process. Fourth is alkaline stability. The most commonly used cationic structure for OH⁻ conducting polymers is the quaternary ammonium group. These groups with β-H are vulnerable to degradation via Hofmann elimination. Even with no β-H, S₂N₂ nucleophilic substitution can still occur. Increasing the steric hindrance around the vulnerable sites can hinder this degradation. Based on the considerations above, the target structure shown (Figure 1) was designed, with a synthetic pathway depicted in Scheme 1.

![Figure 1](image-url)  
**Figure 1.** Structural design of the OH⁻ conducting polymer, qPPO.
Scheme 1. The synthetic pathway of qPPO.

PPO was chosen as the backbone since it is easily functionalized. In this structure (Figure 1), the ether O and the tertiary amine N are hydrogen bond acceptors. The tertiary amine groups are protonated at low pH and in the free base state at high pH, which allows dissolution and membrane casting from low pH aqueous solutions, with lack of water solubility (and thus protection from dissolution) in the high pH operating condition. The structure has no aforementioned β-H’s and the methyl groups (red) vulnerable to S<sub>N</sub>2 attack are shielded by relatively large steric hindrance. All steps resulted in a high yield of ≥ 90%. Due to the steric hindrance, the highly active methylating agent, trimethyloxonium tetrafluoroborate, was required to quaternize the attached tertiary amine group, resulting in a 70% degree of quaternization determined via NMR (Figure S3, corresponding to 4.26 mequiv g<sup>−1</sup> IEC).

The classic way to introduce quaternary ammonium groups is by the polymer benzyl halogenation or aryl chloromethylation, followed by amination using trimethylamine. However, by simply changing the trimethylamine to dimethylamine, one could not obtain tertiary amine groups without the side reaction, in which the dimethylamine reacts with two halogenated benzyl groups to form a quaternary ammonium crosslink. Tomoi and co-workers demonstrated that an n-alkyl chain with more than three carbon centers enhanced the alkaline stability of the cation group. However, the non-polar alkyl chain would lead to lower solubility of the polycation in PVA. To counteract this effect, more polar groups would need to be introduced to the polycation. It is very interesting to design and synthesize new polycations in this direction in the future.
3.2 Membrane morphology

qPPO is highly soluble in aqueous solution at pH < 2 (HBF₄ acid), which allows it to form a homogeneous aqueous solution with PVA. To prevent the dissolution of PVA and enhance the mechanical strength of the membranes, the water-soluble crosslinking agent glutaraldehyde was also added. Once drop-cast from aqueous solution, glutaraldehyde formed acetal crosslinks between PVA chain segments catalyzed by acid₃⁶; the resulting crosslinks were stable under basic conditions. Crosslinking has also been reported to reduce the oxygen permeability of PVA membranes.³⁷ The resulting semi-IPN is illustrated in Figure 2.

![Diagram of semi-IPN](image)

**Figure 2.** Design principles of the polymer composite system. Illustration of the semi-IPN of covalently crosslinked PVA and linear qPPO, and the hydrogen bonds between PVA and qPPO as well as PVA itself. (The semi-IPN schematic is modified from a reference³⁸)

Membranes of varying composition with respect to qPPO and PVA were fabricated, and the homogeneity and miscibility of these polymers was investigated with AFM phase imaging (Figure 3). For the membranes with 0%-30% qPPO (100%-70% PVA), the images show the presence of a single phase, indicating that qPPO and PVA are miscible with each other at these compositions. This can be attributed to the hydrogen bonds between the two polymers, given the presence of electronegative heteroatoms on qPPO and the high density of alcohol groups on PVA. When the concentration of qPPO was further increased, two phases were observed, implying that polymer separation occurred (40%-70%). Here, there is a PVA-rich phase and a qPPO-rich phase. When qPPO is ≥ 80%, the two polymers become miscible again as the qPPO phase dominates. These membranes with ≥ 80% qPPO were too delicate to handle physically and exhibited poor
mechanical properties since they are primarily composed of highly brittle qPPO (typical for membranes with high IECs\textsuperscript{39}), and so are not practical for use in electrolysis cells.

![AFM phase images of qPPO-PVA membranes with different qPPO weight percentage.](image)

**Figure 3.** AFM phase images of the qPPO-PVA membranes with different qPPO weight percentage.

### 3.3 Separator capability

The ability of the membranes to block electrolyte was tested using an H-cell, in which the membrane was separating a chamber filled with 6 M KOH and an empty chamber for 5 days. An ideal membrane should block the liquid solution flowing into the empty chamber so that the chamber remains dry. Membranes with \( \leq 10\% \) qPPO failed this test due to the high proportion of highly hydrophilic PVA, and the ones with \( \geq 20\% \) qPPO passed the test. Therefore, the membranes that were most suitable for alkaline water electrolysis application are those with a composition of 20\%-70\% qPPO.

### 3.4 Ion-exchange capacity & water uptake
The IECs of these membranes were calculated both from the NMR-determined degree of quaternization of qPPO and measurements from back-titration. As can be seen in Table 1, both methods were highly in agreement. The water uptake increases with increasing amounts of PVA, likely because PVA is more hydrophilic than qPPO. This trend is similar to the one reported by T. Xu and co-workers for their PVA-blended anion-exchange membranes.25

| qPPO wt% | PVA wt% | IEC (mequiv g⁻¹) | Water Uptake (%) |
|----------|---------|-------------------|------------------|
|          |         | Theoreticalᵃ      | Measured         |
| 20       | 80      | 0.85              | 0.85             | 79               |
| 30       | 70      | 1.28              | 1.29             | 67               |
| 40       | 60      | 1.70              | 1.63             | 62               |
| 50       | 50      | 2.13              | 2.19             | 59               |
| 60       | 40      | 2.56              | 2.66             | 52               |
| 70       | 30      | 2.98              | 2.87             | 45               |

ᵃ Calculated from the degree of quaternization of qPPO determined by NMR.

3.5 Ion transport properties

An H-cell was used in the through-plane conductivity measurement, with electrodes in basic solution inducing current in order to demonstrate membrane performance under alkaline water electrolysis conditions. The voltage drop due to membrane resistance was measured while hydrogen and oxygen were produced, and thus the conductivity calculated from the voltage drop directly reflects the energy efficiency of the membranes for our targeted application. The OH⁻ conductivity of qPPO-PVA membranes as a function of composition is shown in Figure 4. The membrane with 30% qPPO has a OH⁻ conductivity of 151 mS/cm, which is 2.7 times as high as the proton conductivity of Nafion ((56.4 ± 2.8) mS/cm) and 6.5 times as high as the OH⁻ conductivity of Neosepta AHA AEM ((23.2 ± 1.0) mS/cm) measured under the same conditions. With the same thickness, our membrane can reduce energy losses in water electrolysis due to ion conduction by the same factors. Current density from 0 up to an extremely high value of 1.0 A/cm² was applied. The voltage drop (or the electric field) across the membrane increased linearly with
increasing current density over the whole range of 0-1.0 A/cm² (Figure S5), which indicated that the membrane also conducted OH⁻ well at high current density.

Essentially, conductivity decreases with qPPO content, which is counterintuitive given that qPPO is the functional component for anion transport. For lower qPPO loadings (20%-30%), only a miscible qPPO-PVA (PVA-rich) phase exists (Figure 3), and so it is possible that the resulting structure formed in this phase possesses higher OH⁻ conductivity compared to a qPPO-rich phase.

The perm-selectivity of membranes as a function of qPPO/PVA composition is also shown in Figure 4. Membranes with more PVA have lower perm-selectivity, which confirms that the high ionic conductivity of membranes with lower qPPO content is in part the result of significant K⁺ crossover. There is therefore a trade-off between conductivity and perm-selectivity, whereas the conductivity is granted by the marriage of qPPO ion-exchange capabilities and Grotthuss transport by PVA in the qPPO-PVA (PVA-rich) phase formed, while qPPO alone produces a degree of perm-selectivity to the membrane. Membranes with ≥ 30% qPPO have high perm-selectivities of ≥ 0.92, which makes it possible to integrate them into applications where perm-selectivity is critical, such as bipolar membranes. These membranes have received great interest recently⁴⁰,⁴¹ because they allow the H₂ evolution reaction to proceed under favorable acidic conditions, while at the same time maintaining the O₂ evolution reaction under favorable basic conditions. High perm-selectivity of the AEM is necessary to maintain the desired pH gradient.
Figure 4. Ion transport properties as a function of qPPO weight percentage. (a) OH\textsuperscript{−} conductivity of the qPPO-PVA semi-IPN membranes compared to the proton conductivities of Nafion 117 (in 30% H\textsubscript{2}SO\textsubscript{4}) and the OH\textsuperscript{−} conductivity of Neosepta AHA AEM. (b) OH\textsuperscript{−} perm-selectivity (vs. K\textsuperscript{+}) of the membranes.

3.6 OH\textsuperscript{−} transport mechanism

In the qPPO-PVA (PVA-rich) phase, we hypothesize that the –OH groups in PVA can facilitate the Grotthuss mechanism for OH\textsuperscript{−} conduction (Figure 5a) similar to OH\textsuperscript{−} transport in water, which has a very high conductivity. Here, OH\textsuperscript{−} ions are considered as “proton holes.” OH\textsuperscript{−} movements in one direction is equivalent to protons moving in the opposite direction. In our polymer system, we hypothesize that the PVA-mediated Grotthuss conduction involves three types of reactions: the deprotonation of a PVA –OH by a OH\textsuperscript{−} (type 1), then a series of proton hopping steps from one PVA –OH to its neighboring PVA –O\textsuperscript{−} (type 2); finally, a PVA –O\textsuperscript{−} obtains a proton from H\textsubscript{2}O to reproduce a OH\textsuperscript{−} (type 3). Under an electric field, the net result is that OH\textsuperscript{−} moves in the opposite direction of the field. Several pieces of evidence suggest that this hypothesis is valid. PVA has a pK\textsubscript{a} close to that of water (15.74 vs. 14.0) and other hydrocarbon alcohols such as methanol and ethanol, which have pK\textsubscript{a}s of 15.54 and 16 respectively\textsuperscript{42}. The steps illustrated in Figure 5a therefore have equilibrium constants close to 10\textsuperscript{0}, rendering the reversibility possible. A drop of 10 wt% PVA solution in H\textsubscript{2}O was added into and mixed with 0.1 M NaOD solution in
D$_2$O at room temperature. The mixture was then characterized by H-NMR immediately. No distinct proton peak from PVA–OH was observed (Figure S6), indicating that the proton exchange between PVA–OH and HDO/OH$^-$ was fast and thus the signals of the three were averaged out. Therefore, type 1 and type 3 reactions are possible. The type 2 reaction involves switching from a hydrogen bond to a covalent bond, so that the proton hops through the hydrogen bond network of PVA. The FTIR spectrum of the semi-IPN membrane with 30 wt% qPPO (Figure S7) shows a broad absorption band between 3200 cm$^{-1}$ and 3500 cm$^{-1}$ (instead of a sharp peak at ~3700 cm$^{-1}$), which is evidence of rich O⋯H − O hydrogen bonding.$^{43}$ Therefore, the hypothesis for the type 2 process is reasonable.

A conductivity vs. temperature experiment was conducted for the 30% qPPO membrane to demonstrate that the Grotthuss mechanism as described above exists. The conductivity increased with increasing temperature and reached 284 mS/cm at 50 °C. The activation energy ($E_a$) of ion transport was calculated to be ($14.9 \pm 0.6$) kJ/mol by linear fitting the Arrhenius plot (Figure 5b), which is close to the $E_a$ of Grotthuss modulated OH$^-$ transport ($13.5$ kJ/mol) and lower than the $E_a$ of water (experimental, $20.2$ kJ/mol; simulation, $20.8$ kJ/mol$^{44}$) and F$^-$ (experimental, $20.5$ kJ/mol)$^{44}$ self-diffusion reported for a OH$^-$ conducting membrane in the literature. Therefore, the OH$^-$ conduction may have a Grotthuss component in addition to vehicular transport. In the qPPO-rich phase, the concentration of PVA is low and the water uptake would also be low since qPPO is less hydrophilic than PVA. Therefore, the concentration of sites to aid in ion transport diminishes. It is also possible that the presence of two phases, as observed for 40%–70% qPPO membranes, blocks efficient transport of ions by forming terminated ionic domains.$^{46}$ Lastly, when the concentration of PVA is high, the membrane is very hydrophilic and part of the conductivity is due to water diffusion, which can carry both OH$^-$ and K$^+$ across the membrane. In this case, the concentration of fixed cations at the lowest qPPO weight fraction is low and so fewer K$^+$ ions are blocked.
Figure 5. (a) The OH⁻ transport facilitated by PVA via Grotthuss mechanism. (b) The Arrhenius plot of the conductivity of the 30% qPPO membrane from 10 °C to 50 °C.

3.7 Mechanical properties

Since resistance is proportional to membrane thickness (should conductivity be independent of thickness), membranes that are thin but can perform gas-blocking functions and are able to withstand mechanical impact such as vigorous bubbling and rapid ion transport under working conditions are desired. High ultimate tensile strength allows thinner membranes to be utilized for electrolysis applications, and reasonably large elongation-at-break value is also required, which means the membrane should not be too brittle. The measured ultimate tensile strength and elongation-at-break as a function of membrane composition is displayed in Figure 6a and 6b, respectively. Both of these properties decrease with increasing amount of qPPO, likely a result of the increasing brittle nature of the composite with increasing qPPO, which is highly ionic and is not reinforced by crosslinking like PVA. The ultimate tensile strength and elongation at
break are both lower in the wet state than the dry state, as anticipated. Nevertheless, the membranes with ≥ 70% PVA are still stronger than wet Nafion 117 membranes\textsuperscript{47} because the PVA was also covalently crosslinked. Crosslinked samples are much stronger than the unmodified samples. For the 30% qPPO membranes, the crosslinked membranes have a tensile strength of (126 ± 10) MPa in the dry state, while the uncrosslinked membranes are (52 ± 4) MPa; in the wet state, the crosslinked ones have a tensile strength of (41 ± 5) MPa much higher than the uncrosslinked ones’ (6.5 ± 0.7) MPa. For comparison, the commercial Neosepta AHA anion-exchange membrane, which is reinforced with porous textile support layers, has a tensile strength of (28 ± 3) MPa and (28 ± 2) MPa when dry and wet, respectively. Our 30% qPPO membrane clearly outperforms it in mechanical robustness.

Typical stress-strain curves of the dry and wet 30% qPPO membranes are shown in Figure 6c. With increasing strain, the slope (tangent modulus) under both conditions first increases, reaches a maximum, then decreases. At the beginning, the stress is mainly breaking the weaker van der Waals interactions and hydrogen bonds, followed by breaking the stronger covalent bonds, corresponding to the slope increase. As the stress is further increases, the crosslinked network gradually fails, resulting in the slope decrease. In the dry state, the tangent modulus reaches a maximum of 2.82 GPa at 1.82% strain and 31.5 MPa stress; in the wet state, the tangent modulus reaches a maximum of 1.25 GPa at 0.58% strain and 4.73 MPa stress.
Figure 6. Mechanical properties as a function of qPPO weight percentage. (a) Ultimate tensile strength of the qPPO-PVA semi-IPN membranes in the dry and the wet states compared to Nafion 117. (b) Elongation-at-break of the qPPO-PVA membranes. (c) Typical stress-strain curves of dry and wet 30% qPPO membranes; the crosses are where the tangent moduli (slopes) reach their maxima.

3.8 Comparison with other membranes
Due to the solution-processibility of both qPPO and PVA components, the overall performance of the membranes can be easily optimized by tuning the qPPO-to-PVA ratio. The membrane with 30% qPPO (circled in the Figure 4 plots) has a very high conductivity of 151 mS/cm (at room temperature), which is significantly higher than Nafion 117 (78 mS/cm at 100% R.H., 56.4 mS/cm in 30% H₂SO₄ measured in an H-cell) and Neosepta AHA anion-exchange membranes (23.2 mS/cm in 6 M KOH measured in an H-cell). It also has very high ultimate tensile strengths of 126 MPa (dry) and 41 MPa (wet), which are superior to Nafion 117 (43 MPa (dry) and 34 MPa (wet)).

Insight into the role of PVA can be gained by comparing our membrane to the OH⁻-conducting membrane developed by Hickner and coworkers, which is a semi-IPN of crosslinked poly(ethylene glycol) (PEG) and quaternized PPO. Our membrane displays much higher OH⁻ conductivity (151 mS/cm vs. 29.0 mS/cm at room temperature) and tensile strength (126 MPa vs. 36.4 MPa (dry), 41 MPa vs. 17.4 MPa (wet)) than this PEG-based membrane due to some fundamental differences between PVA and PEG. Unlike PVA, PEG cannot facilitate OH⁻ conduction via Grotthuss mechanism because the ether –O– in PEG is far less basic than the alkoxide –O⁻ ion along the PVA backbone under basic conditions, and therefore cannot support proton exchange with H₂O to regenerate OH⁻, which may be the main reason for its lower OH⁻ conductivity. PEG cannot form hydrogen bonds with itself or the polycation, while PVA can form hydrogen bonds with both itself and qPPO, giving our membrane higher strength.

The exceptional performance of this membrane compared to others is highlighted in Figure 7. Based on these findings, a relatively thin membrane can be utilized, and together with excellent OH⁻ conductivity, the sheet resistance is very low such that alkaline water electrolysis could be made more energy efficient. The anion perm-selectivity value (0.92) and the elongation-at-break values (12.0% (dry) and 9.3% (wet)) are also both favorable features.
Figure 7. The conductivity (at ambient temperature) and tensile strength of the 30% qPPO/70% PVA semi-IPN membrane in this work in comparison with those of Nafion 117, Neosepta AHA AEM, SIPN-60-2\textsuperscript{49} and HMT-PMBI AEM\textsuperscript{50}.

3.9 Alkaline stability

In addition to transport and mechanical features, the chemical stability of a membrane with 30% qPPO was evaluated. We performed water electrolysis in an H-cell at a current density of 0.13 A/cm\textsuperscript{2} (per membrane area) at room temperature with 6 M KOH electrolyte (replaced by new solutions every 6 hours), and measured its conductivity in the same H-cell every two days. It showed little change in conductivity over a period of 10 days (Figure S8), and the perm-selectivity also did not decrease significantly (0.92 ± 0.01 to 0.90 ± 0.01) at the end. To test this further, the quaternary ammonium cations on qPPO that are the most vulnerable to alkaline degradation were tested by immersing a 100% qPPO membrane in excess 6 M KOH at room temperature ((22 ± 1 °C) over a period of 10 days. The proton NMR spectrum of the polymer was almost unchanged after the KOH test (Figure S9). Its degree of quaternization decreased just slightly from 70% to 68% (from NMR), which explains the slight decrease in perm-selectivity. As hypothesized, the relatively high stability of the membrane in concentrated base is due to the choice of stable chemical structure as well as its incorporation with a crosslinked support polymer designed herein. The large steric hindrance around the quaternary ammonium groups and absence of β-H’s lower
the degradation rate of qPPO, and the acetal crosslinks of PVA are well known to be stable under basic conditions.

Conclusions

A OH\textsuperscript{-} conducting polymer composite system was designed, synthesized, and optimized in terms of composition of parent polymers (30\% qPPO) to obtain the extraordinary conductivity (151 mS cm\textsuperscript{-1}), mechanical properties (126 MPa, dry and 41 MPa, wet ultimate tensile strength, 12\% elongation-at-break), perm-selectivity (0.92), and chemical stability in alkaline solution (10 day constant exposure with little loss in conductivity and perm-selectivity), proving its use in practical alkaline electrolysis. The high OH\textsuperscript{-} conductivity is, to the best of our knowledge, the highest achieved for a stable, perm-selective membrane, which will improve energy efficiency in water electrolysis. It was found that the optimal membrane (30\% qPPO/70\% PVA) contained only one phase, indicating that at this composition the polymers are miscible and form a structure that is optimal for OH\textsuperscript{-} conduction, which is attributed to added conductivity along the high-density – OH groups on PVA, while qPPO ion-exchange features largely reject cation crossover, showing great potential for bipolar membrane applications. The design resulting in high OH\textsuperscript{-} conductivity is a polymer analogue inspired by the high OH\textsuperscript{-} mobility in aqueous solutions of strong bases—an anion exchange polymer (strong base) was dissolved in PVA (water analogue). This results in Grotthuss-like conduction along with mechanical robustness, as the covalently crosslinked PVA forms hydrogen bonds with the anion exchange polymer as well as with itself.

We expect that the OH\textsuperscript{-} conductivity and the mechanical properties could be further improved by optimizing the degree of quaternization of qPPO and the degree of crosslinking of PVA. To affirm product separation capabilities, this property should be directly measured. Moreover, the membrane performance at elevated temperature, without supporting electrolyte,\textsuperscript{51} at a higher current density, and in membrane-electrode assembly configuration should be evaluated. Due to the similarity in components and configuration and desire for the same properties, this membrane system could also be applied to alkaline fuel cells, in addition to bipolar membranes, as already mentioned. Future studies could confirm this membrane’s performance under conditions specific to such analogous systems.
Supporting Information

NMR spectra of PPO-NH₂, PPO-NMe₂, and qPPO; illustration of the H-cell; OH⁻ conduction at high current density; NMR and FTIR spectra as evidence of Grotthuss conduction; alkaline stability of the membrane

Conflicts of Interest

There are no conflicts of interest to declare.

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References

(1) Lipman, T. An overview of hydrogen production and storage systems with renewable hydrogen case studies, DOE, 2011.

(2) Carmo, M.; Fritz, D. L.; Mergel, J.; Stolten, D. A Comprehensive Review on PEM Water Electrolysis. Int. J. Hydrog. Energy 2013, 38, 4901-4934.

(3) Wu, X.; Scott, K. Cu₅Co₃₋ₓO₄ (0 ≤ x ≤ 1) Nanoparticles for Oxygen Evolution in High Performance Alkaline Exchange Membrane Water Electrolysers. J. Mater. Chem. 2011, 21, 12344-12351.

(4) Verlage, E.; Hu, S.; Liu, R; Jones, R. J. R.; Sun, K.; Xiang, C.; Lewis, N. S.; Atwater, H. A. A Monolithically Integrated, Intrinsically Safe, 10% Efficient, Solar-Driven Water-Splitting System
Based on Active, Stable Earth-Abundant Electrocatalysts in Conjunction with Tandem III–V Light Absorbers Protected by Amorphous TiO$_2$ Films. *Energy Environ. Sci.* **2015**, *8*, 3166-3172.

(5) McCrory, C. C. L.; Jung, S.; Ferrer, I. M.; Chatman, S. M.; Peters, J. C.; Jaramillo, T. F. Benchmarking Hydrogen Evolving Reaction and Oxygen Evolving Reaction Electrocatalysts for Solar Water Splitting Devices. *J. Am. Chem. Soc.* **2015**, *137*, 4347-4357.

(6) McCrory, C. C. L.; Jung, S.; Peters, J. C.; Jaramillo, T. F. Benchmarking Heterogeneous Electrocatalysts for the Oxygen Evolution Reaction. *J. Am. Chem. Soc.* **2013**, *135*, 16977-16987.

(7) Hernandez-Pagan, E. A.; Vargas-Barbosa, N. M.; Wang, T.; Zhao, Y.; Smotkin, E. S.; Mallouk, T. E. Resistance and Polarization Losses in Aqueous Buffer-Membrane Electrolytes for Water-Splitting Photocatalyst cells. *Energy Environ. Sci.* **2012**, *5*, 7582-7589.

(8) Liu, Z.; Sajjad, S. D.; Gao, Y.; Yang, H.; Kaczur, J. J.; Masel, R. I. The Effect of Membrane on an Alkaline Water Electrolyzer. *Int. J. Hydrog. Energy* **2017**, *42*, 29661-29665.

(9) Faraj, M.; Boccia, M.; Miller, H.; Martini, F.; Borsacchi, S.; Geppi, M.; Pucci, A. New LDPE Based Anion-Exchange Membranes for Alkaline Solid Polymeric Electrolyte Water Electrolysis. *Int. J. Hygrogen Energ.* **2012**, *20*, 14992-15002.

(10) Xiao, L.; Zhang, S.; Pan, J.; Yang, C.; He, M.; Zhuang, L.; Lu, J. First Implementation of Alkaline Polymer Electrolyte Water Electrolysis Working Only with Pure Water. *Energy Environ. Sci.* **2012**, *5*, 7869-7871.

(11) Leng, Y.; Chen, G.; Mendoza, A. J.; Tighe, T. B.; Hickner, M. A.; Wang, C.-Y. Solid-State Water Electrolysis with an Alkaline Membrane. *J. Am. Chem. Soc.* **2012**, *134*, 9054-9057.

(12) Parrondo, J.; Arges, C. G.; Niedzwiecki, M.; Anderson, E. B.; Ayers, K. E.; Ramani, V. Degradation of Anion Exchange Membranes Used for Hydrogen Production by Ultrapure Water Electrolysis. *RSC Adv.* **2014**, *4*, 9875-9879.

(13) Park, E. J.; Capuano, C. B.; Ayers, K. E.; Bae, C. Chemically Durable Polymer Electrolytes for Solid-State Alkaline Water Electrolysis. *J. Power Sources* **2018**, *375*, 367-372.
(14) Varcoe, J. R.; Atanassov, P.; Dekel, D. R.; Herring, A. M.; Hickner, M. A.; Kohl, P. A.; Kucernak, A. R.; Mustain, W. E.; Nijmeijer, K.; Scott, K.; Xu, T.; Zhuang, L. Anion-Exchange Membranes in Electrochemical Energy Systems. *Energy Environ. Sci.* **2014**, *7*, 3135-3191.

(15) Zeng, K.; Zhang, D. Recent Progress in Alkaline Water Electrolysis for Hydrogen Production and Applications. *Prog. Energy Combust. Sci.* **2010**, *36*, 307-326.

(16) Tuckerman, M. E.; Marx, D.; Parrinello, M. The Nature and Transport Mechanism of Hydrated Hydroxide Ions in Aqueous Solution. *Nature* **2002**, *417*, 925-929.

(17) Vandiver, M. A.; Caire, B. R.; Carver, J. R.; Waldrop, K.; Hibbs, M. R.; Varcoe, J. R.; Herring, A. M.; Liberatore, M. W. Mechanical Characterization of Anion Exchange Membranes by Extensional Rheology under Controlled Hydration. *J. Electrochem. Soc.* **2014**, *161*, H677-H683.

(18) Yan, X.; He, G.; Gu, S.; Wu, X.; Du, L.; Zhang, H. Quaternized Poly(ether ether ketone) Hydroxide Exchange Membranes for Fuel Cells. *J. Membr. Sci.* **2011**, *375*, 204-211.

(19) Luo, Y.; Guo, J.; Wang, C.; Chu, D. Fuel Cell Durability Enhancement by Crosslinking Alkaline Anion Exchange Membrane Electrolyte. *Electrochem. Commun.* **2012**, *16*, 65-68.

(20) Wu, Y.; Wu, C.; Xu, T.; Yu, F.; Fu, Y. Novel Anion-Exchange Organic-Inorganic Hybrid Membranes: Preparation and Characterizations for Potential Use in Fuel Cells. *J. Membr. Sci.* **2008**, *321*, 299-308.

(21) Zhao, Y.; Pan, J.; Yu, H.; Yang, D.; Li, J.; Zhuang, L.; Shao, Z.; Yi, B. Quaternary Ammonia Polysulfone-PTFE Composite Alkaline Anion Exchange Membrane for Fuel Cells Application. *Int. J. Hydrog. Energy* **2013**, *38*, 1983-1987.

(22) Price, S. C.; Ren, X.; Jackson, A. C.; Ye, Y.; Elabd, Y. A.; Beyer, F. L. Bicontinuous Alkaline Fuel Cell Membranes from Strongly Self-Segregating Block Copolymers. *Macromolecules* **2013**, *46*, 7332-7340.

(23) Li, Q.; Liu, L.; Miao, Q.; Jin, B.; Bai, R. Hydroxide-Conducting Polymer Electrolyte Membranes from Aromatic ABA Triblock Copolymers. *Polym. Chem.* **2014**, *5*, 2208-2213.

(24) He, Y.; Pan, J.; Wu, L.; Zhu, Y.; Ge, X.; Ran, J.; Yang, Z. J.; Xu, T. A Novel Methodology to Synthesize Highly Conductive Anion Exchange Membranes. *Sci. Rep.* **2015**, *5*, 13417.
(25) Wu, Y.; Luo, J.; Zhao, L.; Zhang, G.; Wu, C.; Xu, T. QPPO/PVA Anion Exchange Hybrid Membranes from Double Crosslinking Agents for Acid Recovery. *J. Membr. Sci.* **2013**, *428*, 95-103.

(26) Suzuki, A.; Murakami, T. High-Strength Poly(Vinyl Alcohol) Hydrogels for Artificial Cartilage. *Encyclopedia of Biocolloid and Biointerface Science 2V Set* **2016**, *21*, 269-277.

(27) Hibbs, M. R.; Hickner, M. A.; Alam, T. M.; McIntyre, S. K.; Fujimoto, C. H.; Cornelius, C. J. Transport Properties of Hydroxide and Proton Conducting Membranes. *Chem. Mater.* **2008**, *20*, 2566-2573.

(28) Geise, G. M.; Hickner, M. A.; Logan, B. E. Ionic Resistance and Permselectivity Tradeoffs in Anion Exchange Membranes. *ACS Appl. Mater. Interfaces* **2013**, *5*, 10294-10301.

(29) Kielland, J. Individual Activity Coefficients of Ions in Aqueous Solutions. *J. Am. Chem. Soc.* **1937**, *59*, 1675-1678.

(30) Wright, A. G.; Weissbach, T.; Holdcroft, S. Poly(phenylene) and *m*-Terphenyl as Powerful Protecting Groups for the Preparation of Stable Organic Hydroxides. *Angew. Chem. Int. Ed.* **2016**, *55*, 4818-4821.

(31) Ran, J.; Wu, L.; Ru, Y.; Hu, M.; Din, L.; Xu, T. Anion Exchange Membranes (AEMs) Based on Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and its derivatives. *Polym. Chem.* **2015**, *6*, 5809-5826.

(32) Xu, T.; Wu, D.; Wu, L. Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO)—A Versatile Starting Polymer for Proton Conductive Membranes (PCMs). *Prog. Polym. Sci.* **2008**, *33*, 894-915.

(33) Schauer, J.; Hnát, J.; Brožová, L.; Žitka, J.; Bouzek, K. Anionic Catalyst Binders Based on Trimethylamine-Quaternized Poly(2,6-dimethyl-1,4-phenylene oxide) for Alkaline Electrolyzers. *J. Membr. Sci.* **2015**, *473*, 267-273.

(34) Gopi, K. H.; Peera, S. G.; Bhat, S. D.; Sridhar, P.; Pitchumani, S. Preparation and Characterization of Quaternary Ammonium Functionalized Poly(2,6-dimethyl-1,4-phenylene oxide) as Anion Exchange Membrane for Alkaline Polymer Electrolyte Fuel Cells. *Int. J. Hydrog. Energy* **2014**, *39*, 2659-2668.
(35) Tomoi, M.; Yamaguchi, K.; Ando, R.; Kantake, Y.; Aosaki, Y.; Kubota, H. Synthesis and Thermal Stability of Novel Anion Exchange Resins with Spacer Chains. *J. Appl. Polym. Sci.* **1998**, *64*, 1161-1167.

(36) Bolto, B.; Tran, T.; Hoang, M.; Xie, Z. Crosslinked Poly(vinyl alcohol) Membranes. *Prog. Polym. Sci.* **2009**, *34*, 969-981.

(37) Figueiredo, K. C. S.; Alves, T. L. M.; Borges, C. P. Poly(vinyl alcohol) Films Crosslinked by Glutaraldehyde under Mild Conditions. *J. Appl. Polym. Sci.* **2009**, *111*, 3074-3080.

(38) Ye, Y.-S.; Rick, J.; Hwang, B. J. Water Soluble Polymers as Proton Exchange Membranes for Fuel Cells. *Polymers* **2012**, *4*, 913-963.

(39) Hickner, M. A.; Herring, A. M.; Coughlin, E. B. Anion Exchange Membranes: Current Status and Moving Forward. *J. Polym. Sci. Part B Polym. Phys.* **2013**, *51*, 1727-1735.

(40) McDonald, M. B.; Ardo, S.; Lewis, N. S.; Freund, M. S. Use of Bipolar Membranes for Maintaining Steady-State pH Gradients in Membrane-Supported, Solar-Driven Water Splitting. *ChemSusChem* **2014**, *7*, 3021-3027.

(41) Sun, K.; Liu, R.; Chen, Y.; Verlage, E.; Lewis, N. S.; Xiang, C. A. Stabilized, Intrinsically Safe, 10% Efficient, Solar-Driven Water-Splitting Cell Incorporating Earth-Abundant Electrocatalysts with Steady-State pH Gradients and Product Separation Enabled by a Bipolar Membrane. *Adv. Energy Mater.* **2016**, *6*, 1600379.

(42) Ballinger, P.; Long, F. A. Acid Ionization Constants of Alcohols. II. Acidities of Some Substituted Methanols and Related Compounds. *J. Am. Chem. Soc.* **1960**, *82*, 795-798.

(43) Gorman, M. The Evidence from Infrared Spectroscopy for Hydrogen Bonding. *J. Chem. Educ.* **1957**, *34*, 304-306.

(44) Pandey, T. P.; Sarode, H. N.; Yang, Y.; Yang, Y.; Vezzu, K.; Noto, V. D.; Seifert, S.; Knauss, D. M.; Liberatore, M. W.; Herring, A. M. A Highly Hydroxide Conductive, Chemically Stable Anion Exchange Membrane, Poly(2,6 dimethyl 1,4 phenylene oxide)-b-Poly(vinyl benzyl trimethyl ammonium), for Electrochemical Applications. *J. Electrochem. Soc.* **2016**, *163*, H513-H520.
(45) Chen, C.; Tse, Y.-L. S.; Lindberg, G. E.; Knight, C.; Voth, G. A. Hydroxide Solvation and Transport in Anion Exchange Membranes. *J. Am. Chem. Soc.* **2016**, *138*, 991-1000.

(46) Arges, C. G.; Kambe, Y.; Dolejsi, M.; Wu, G.-P.; Segal-Pertz, T.; Ren, J.; Cao, C.; Craig, G. S. W.; Nealey, P. F. Interconnected Ionic Domains Enhance Conductivity in Microphase Separated Block Copolymer Electrolytes. *J. Mater. Chem. A* **2017**, *5*, 5619-5629.

(47) Fuel Cell Store product bulletin P-12.  
http://www.fuelcellstore.com/spec-sheets/chemours-nafion-115-117-1110-spec-sheet.pdf

(48) Yoshisugu, S.; Ekdunge, P.; Simonsson, D. Proton Conductivity of Nafion 117 as Measured by a Four-Electrode AC Impedance Method. *J. Electrochem. Soc.* **1996**, *143*, 1254-1259.

(49) Pan, J.; Zhu, L.; Han, J.; Hickner, M. A. Mechanically Tough and Chemically Stable Anion Exchange Membranes from Rigid-Flexible Semi-Interpenetrating Networks. *Chem. Mater.* **2015**, *27*, 6689-6698.

(50) Wright, A. G.; Fan, J.; Britton, B.; Weissbach, T.; Lee, H.-F.; Kitching, E. A.; Peckham, T. J.; Holdcroft, S. Hexamethyl-p-Terphenyl Poly(benzimidazolium): A Universal Hydroxide-Conducting Polymer for Energy Conversion Devices. *Energy Environ. Sci.* **2016**, *9*, 2130-2142.

(51) Arges, C. G.; Zhang, L. Anion Exchange Membranes’ Evolution toward High Hydroxide Ion Conductivity and Alkaline Resiliency. *ACS Appl. Energy Mater.* **2018**, *1*, 2991-3012.
• Grotthuss OH⁻ conduction
• High tensile strength

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