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Anion Exchange Membranes: Enhancement by Addition of Unfunctionalized Triptycene Poly(Ether Sulfone)s

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Abstract

Anion exchange membrane fuel cells are a clean and efficient promising future energy source. However, the development of stable high performance membranes remains a major challenge. Herein we demonstrate that the addition of unfunctionalized triptycene poly (ether sulfones) into 1-methylimidazolium poly (ether sulfone) enhances membrane's conductivity (up to 0.082 S/cm at 80 °C), minimizes dimensional changes over temperatures from 20 °C to 80 °C, and enhances stability with 30% of the initial conductivity maintained after 450 h. These enhancements appear to be the result of nano-phase separation and internal free volume. Small angle X-ray scattering

and transmission electron microscopy reveal that the internal domain size increases (up to 7.44 nm) with increasing triptycene fraction.

The anion exchange membrane fuel cell (AEMFC) is an electrochemical device that can converts the chemical energy of H2 (or methanol) directly into an electrical current. Interest in anion exchange membrane fuel cells have been driven by the environmentally friendly nature of these systems, the higher oxygen reduction reaction kinetics relative to proton exchange membrane fuel cells, lower methanol permeability through the membranes in alkaline media, and the fact that the earth abundant metals are efficient fuel cell catalysts under basic conditions.[1–3] However, there are impediments to the adoption of AEMFCs. In particular efficiency and stability of the anion exchange membranes (AEMs) remains a weakness. A typical alkaline AEM is composed of a polymer backbone with tethered cationic ion-exchange groups to facilitate the movement of free OH^- ions, while being impermeable to cations. The challenge is to fabricate AEMs with high OH^- ion conductivity and mechanical durability without chemical degradation at elevated temperatures and pH.[4]

Cationic polymers based on poly(arylene ether sulfone), polyphenylenes, polybenzimidazole, poly(epichlorohydrins) and polyethylene have been extensively studied as AEMs.[5–10] Among them, poly(arylene ether sulfone)s (PES) as base polymers have received the most attention due to their excellent thermal, mechanical and chemical stability. Furthermore, a wide range of functionalization chemistry has been developed for these materials and thus, PES has emerged as a versatile candidate for development of AEM.[11] Even though potentially weaker stability is predicted as a result of nucleophilic attack on cation functionalized backbones,[12] numerous efforts on quaternary ammonium with different chemical structures as

cation functional groups have been shown to exhibit alkaline stability and high ion conductivity.[4,13,14] Of these groups, the methyl imidazolium structure is particularly attractive as a result of its OH- conductivity and chemical stability resulting from its five-membered aromatic ring structure. The electronic delocalization within the rings diffuses charge density of a cation and thereby weakens electrostatic interactions with the hydroxide ions to prevent strong pinning and facilitate higher conductivity.[15] Furthermore, the absence of a sp3 environment and β-hydrogens removes the possibility of elimination reactions.[3,16] In order to utilize the imidazolium functional group to its maximum potential in PES, high degrees of functionalization have been pursued. However, at high degrees of functionalization, imidazolium bisphenol A PES (Im-BPAPES) was not mechanically stable as a result of swelling and dissolution. Improvement strategies to create mechanically stable imidazolium containing membranes include the design of comb-shaped polymers,[17] block copolymers,[18,19] and crosslinking.[20] These methods utilize nanoscale hydrophobic/hydrophilic phase separations to drive the formation of interconnected ion conducting channels while maintaining mechanical stability.[21,22]

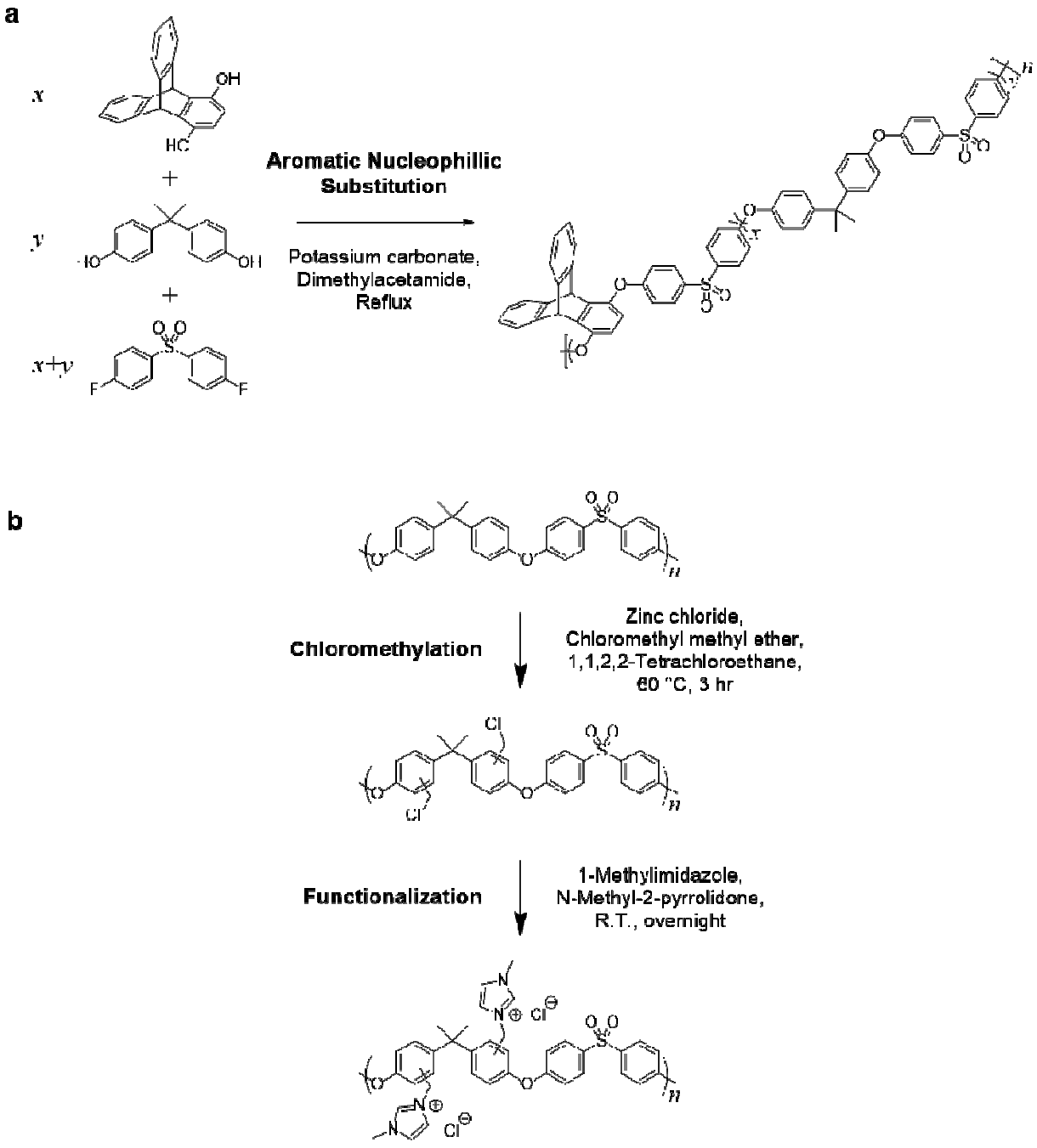
Herein we introduce a new and facile way to enhance ion conductivity, mechanical stability and chemical stability simultaneously by using triptycene-containing PES as an additive. Triptycene is known to enhance polymer properties by the translation of its unique molecular characteristics to bulk systems. Specifically its rigid 3D structure promotes high internal free-volume that prevents dense packing of molecular chains and an interlocked structure, creating materials with high glass transition temperatures and enhanced mechanical properties.[23] Examples of the utility of triptycenes in polymers include creating materials with size exclusion properties and high fluorescence,[24] producing low dielectric constant solids,[25] and the simultaneous enhancement of ductility and stiffness of films and fibers.[26] Our expectation is that

some of these attractive attributes can be transferred to AEMs by blending. This is not the first realization that including triptycenes in a polymer's backbone can improve an anion conducting membrane.[27] However we are taking a different approach by exploring if the addition of an unfunctionalized triptycene PES will improve AEM properties.

High conductivity of hydroxide ions at working temperatures (60-80 °C) are a requirement for viable high-performance fuel cells. The two major parameters which determine hydroxide conductivity of membrane are the ion exchange capacity (IEC) and the internal domain structure that affects ion mobility. In this study, the IEC is designed to be constant for all samples, allowing for a direct observation of the effect of triptycene additives on the ion mobility through changes in the material's internal domain structure. It is generally accepted that increased ion conductivity at higher temperatures is a result of an expansion of the free volume in the polymer membrane.[28] As a result, we rationalized that the addition of free volume promoting triptycene groups in the materials will enhance hydroxide conduction relative to pure Im-BPAPES membranes.

As indicated, BPAPES is an established material from which AEMs were made and hence is well suited to test our hypothesis. Post-polymerization reactions provide randomly-functionalized BPAPES that is expected to have a homogenous solid state structure when made into a film. As a first step, highly chloromethylated BPAPES (Cl-BPAPES) was synthesized (Scheme 1). The degree of chloromethylation was found to be 95% by 1H NMR spectroscopy (Supporting Information Figure S1). Cl-BPAPES was then reacted with 1-methylimidazole to form 1-methylimidazolium BPAPES (Im-BPAPES). Im-BPAPES was cast into a free-standing membrane and repeatedly soaked in fresh solutions of 1.0 M sodium hydroxide to yield an alkaline AEM with OH- ions and an IEC of 2.40 mmol/g (See SI for details of sample

preparation). To study the effect of additives on conductivity and properties of the films, unfunctionalized triptycene containing PES copolymers (TrpPES) as well as unfunctionalized BPAPES were combined with Im-BPAPES in AEMs. By design we have kept the fractional mass of the Im-BPAES constant in all films. In this way, the IEC of the samples are constant, and the effect of additive polymers can be directly observed. To control the free volume introduced by the additives, PESs with five different ratios of bisphenol A and triptycene-1,4,-hydroquinone were used: BPAPES, TrpPES(1,4), TrpPES(1,1), TrpPES(4,1), and TrpPES(1,0) (Scheme 1, Table S1 and Table S2). TrpPES(1,0) contains the most triptycene functional group and it is expected that this material would impart the greatest amount of internal free volume into the membrane. Membranes were formed from solutions containing a fixed mass of Im-BPAPES and the same weight of each additive BPAPES, TrpPES(1,4), TrpPES(1,1), TrpPES(4,1), and TrpPES(1,0). The polymer solutions were then cast to form AEMs with different amounts of triptycene: TRP-0, TRP-20, TRP-50, TRP-80, and TRP-100, respectively (Table S2). Im-BPAPES from a single reaction batch was used to ensure that all five AEMs have the same IECs of 1.83 ± 0.05 mmol/g (See SI for details of sample preparation).



Scheme 1. **a**. Synthesis of TrpPES copolymer. Ratios between *x* and *y* are represented as (*x*,*y*) in TrpPES(*x*,*y*) and five different copolymers were synthesized. The ratios of (0,1), (1,4), (1,1), (4,1) and (1,0) gave BPAPES, TrpPES(1,4), TrpPES(1,1), TrpPES(4,1), and TrpPES(1,0), respectively (Table S1 and S2). **b**. Synthesis of Im-BPAPES copolymer from chloromethylation of BPAPES.

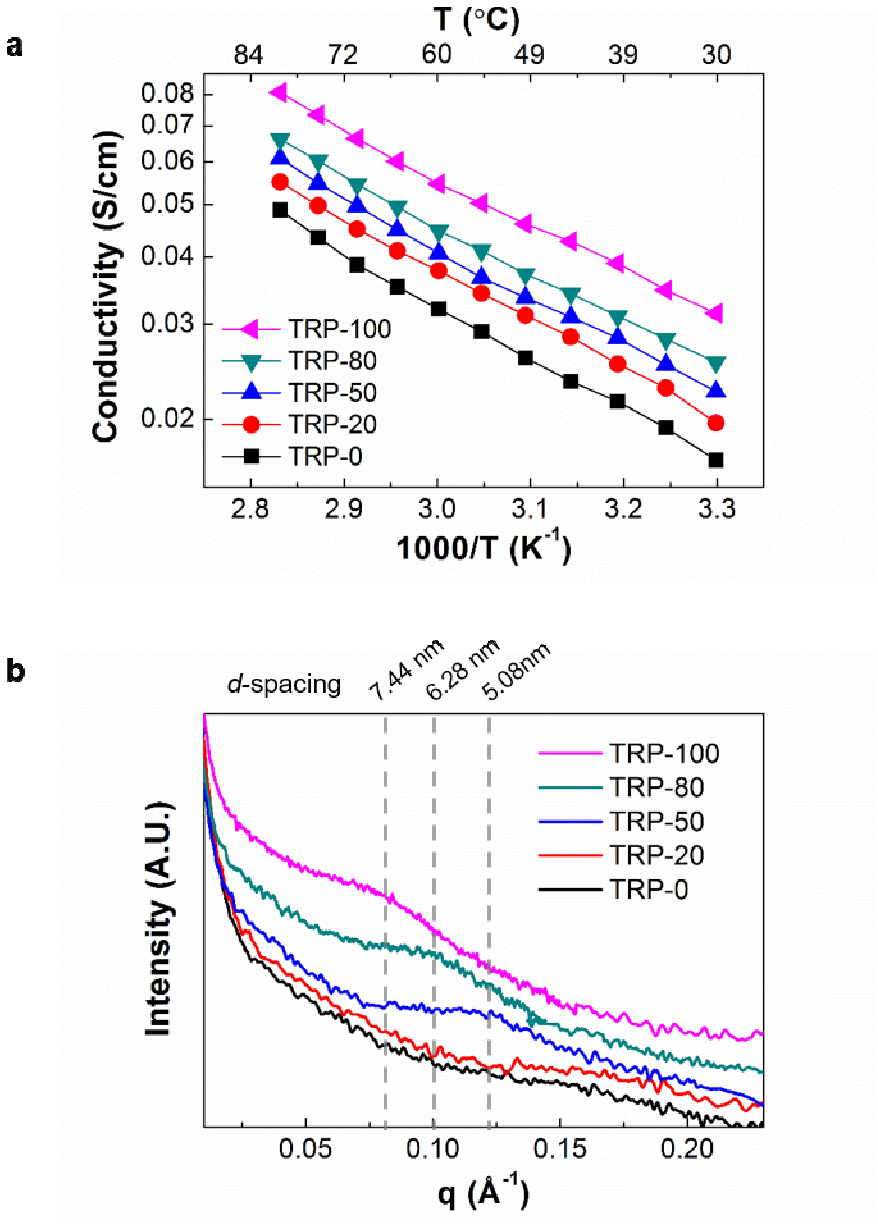


Figure 1. **a**. Temperature dependent conductivity of samples. All samples had IEC of 1.82 ± 0.05 mmol/g. **b**. SAXS spectra of the samples. *d*-spacing values for TRP-50, -80 and -100 were calculated to be 5.08, 6.28 and 7.44 nm.

Temperature-dependent hydroxide conductivities were measured for the different compositions (Figure 1a). Without any triptycene groups in the additive polymer, TRP-0 has a conductivity of 0.018 S/cm at 20 °C. On the other hand, using TrpPES(1,0) as an additive, TRP-100 displayed an increased conductivity of 0.030 S/cm at the same temperature. At a higher

temperature of 80 °C, TRP-100's conductivity is 0.082 S/cm, which is 1.7-times higher than conductivity of TRP-0 at the same temperature. Conductivities of the AEMs at working temperatures (60 – 80 °C) surpassed the required conductivity of 0.05 S/cm that is considered necessary for reliable performance, and the fact that membranes of TRP-100 performed close to 0.1 S/cm which is often regarded as prerequisite for high performance cell output[4] is promising. Furthermore, the TRP-100 AEM displays a higher conductivity than previously reported triptycene poly(arylene ether sulfone)s derived materials with 0.072 S/cm at 80 °C and a higher IEC of 2.61 mmol/g.[27] Our results suggest that balancing free volume and IEC is more important than simply having a higher IEC. Furthermore TRP-100 displays an record conductivity for an AEMs based on BPAPES.[16,29,30] The conduction behavior of the samples over the temperature range of 20 – 80 °C obeyed Arrhenius behavior with the R2 linear regression values in excess of 0.99 for all samples (Figure S3). Activation energies, E_a, which reveal the minimum activation energies for conduction were calculated from the slope of the plot. The activation energy decreases with the increasing content of triptycene moiety showing that hydroxide ion migration is facilitated by this addition. E_a for TRP-100 and TRP-0 were 16.4 and 18.4 kJ/mol, respectively. This improved performance suggests that adding polymer additives with high free volume is a promising method to achieve higher conductivity for anion exchange membranes.

The difference on conductivity and E_a, of the five samples, prompted small-angle X-ray scattering (SAXS) measurements to quantitatively understand internal domain morphologies. SAXS profiles of the samples with higher triptycene contents (TRP-50, TRP-80 and TRP-100) showed a notable peak in the q range of 0.15 – 0.08 Å-1. Those q ranges are for ionomer peaks, arising from the mean correlation spacing between the hydrophilic water-domains and indicate the size of the ionic clusters within the samples.[22] The SAXS data revealed that TRP-100 had

the largest d-spacing, with an internal domain size of 7.44 nm, followed by TRP-80 and TRP-50 at 6.28 and 5.08 nm, respectively (Figure 1b). TRP-20 and TRP-0 had relatively featureless scattering profiles from which we cannot extract a d-spacing data. The differently sized internal domain morphologies seen from SAXS can be directly observed in Transmission Electron Microscopic (TEM) images. The dark and bright parts of the images respectively correspond to stained hydrophilic methylimidazole functionalized domains and hydrophobic domains that include the additives (Figure 2). Addition of hydrophobic additives induced nano-sized hydrophilic/hydrophobic phase separation with TRP-50, TRP-80 and TRP-100 all clearly showing phase separated morphologies. TRP-100 exhibited a much clearer and larger phase separation than TRP-50, and consistent with the SAXS results TRP-0 and TRP-20 did not display morphological patterns. Thus, higher content of unfunctionalized triptycene in the membrane resulted in the development of phase separation with larger hydrophilic internal domain sizes.

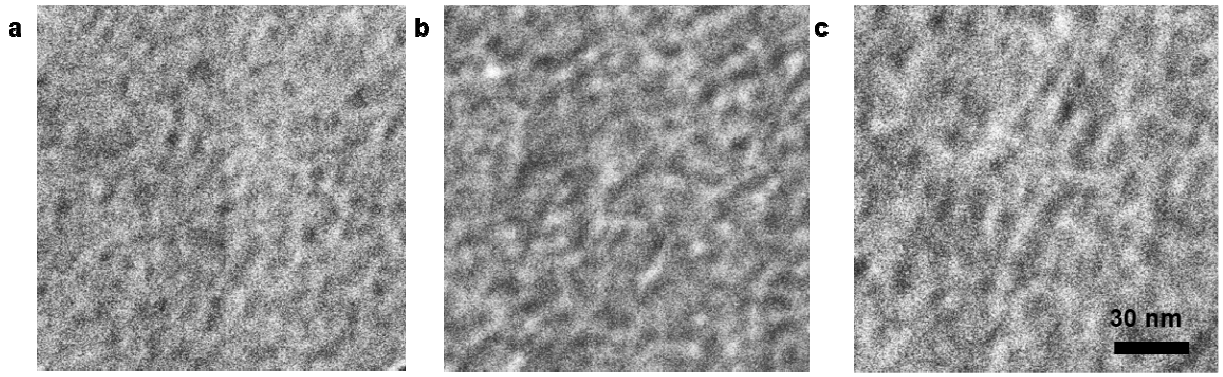


Figure 2. **a**-**c**. TEM images of TRP-50, TRP-80, TRP-100, respectively. Scale for images **a**-**c** is given in **c**.

To further understand the membrane structure and characteristics, water uptake and swelling ratios of the membranes were measured. TRP-0 undergoes a 67% water uptake at 20 °C, whereas TRP-100 takes up 1.6-times more water (Figure 3a). Furthermore, although TRP-0's

water uptake increases 87% with a temperature increase from 20 °C to 80 °C, TRP-100 only undergoes a 37% increase of the full range. We attribute this behavior to increased and stable free volume TRP-100, which allows for domain structures that entrap water in the membrane.

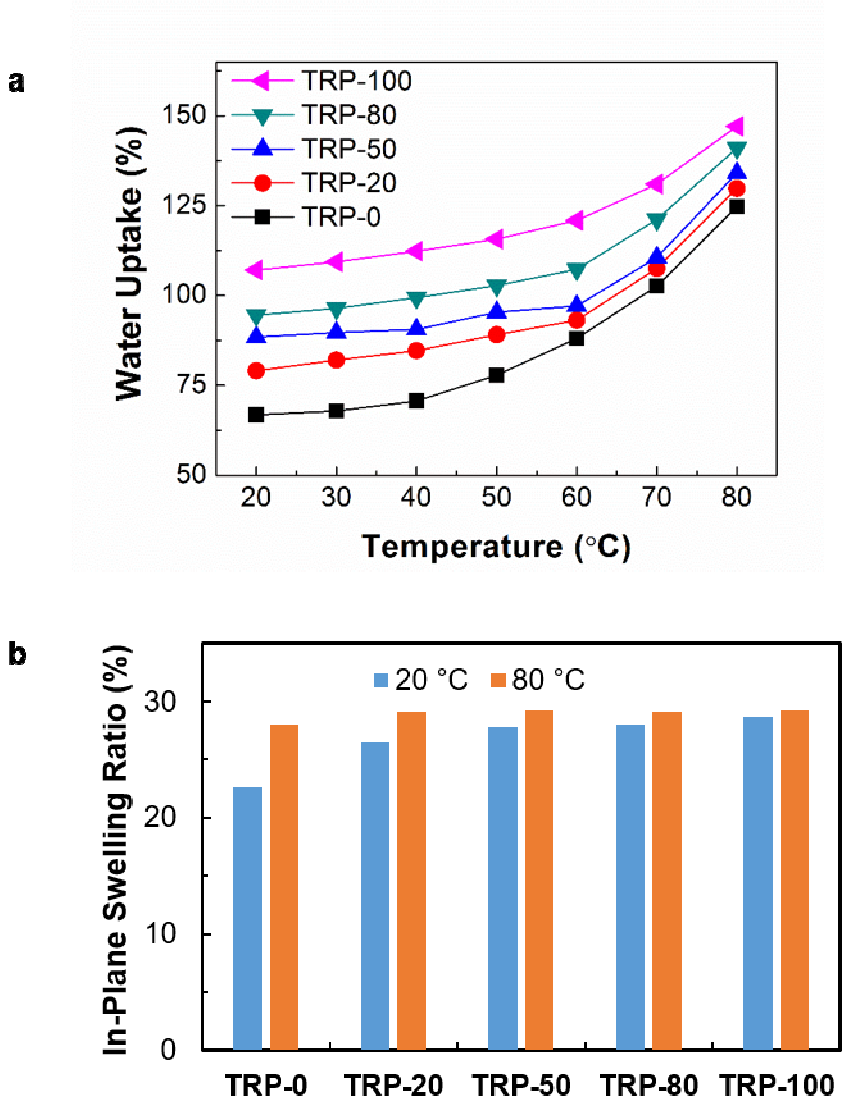


Figure 3. Water uptake (**a**) and in-plane swelling ratio (**b**) of samples in the temperature ranges of 20 °C and 80 °C.

The triptycene additives improve the dimensional stability of the samples. By comparing swelling ratios from a dry reference state relative to the membranes in water at 20 °C and 80 °C, dimensional changes of the membranes at various temperatures were observed. Dimensional

stability is necessary to preserve the integrity of the fuel cell under the changing operating conditions. Corresponding to the water uptake results, TRP-100 had a small change of swelling ratio from 28.7% to 29.2 % for the temperature change from 20 °C to 80 °C (Figure 3b). However, TRP-0 had relatively larger change of 22.6% to 28.0% for the same temperature change. Improved dimensional stability of TRP-100 over TRP-0 is corroborated from mechanical tensile tests wherein TRP-100 has improved tensile strength and a higher Young's modulus relative to TRP-0 (Figure S4 and Table S3). Additionally, the thermal stability of the membranes as determined by thermal gravimetric analysis were not adversely affected by the addition of triptycene additives (Figure S5).

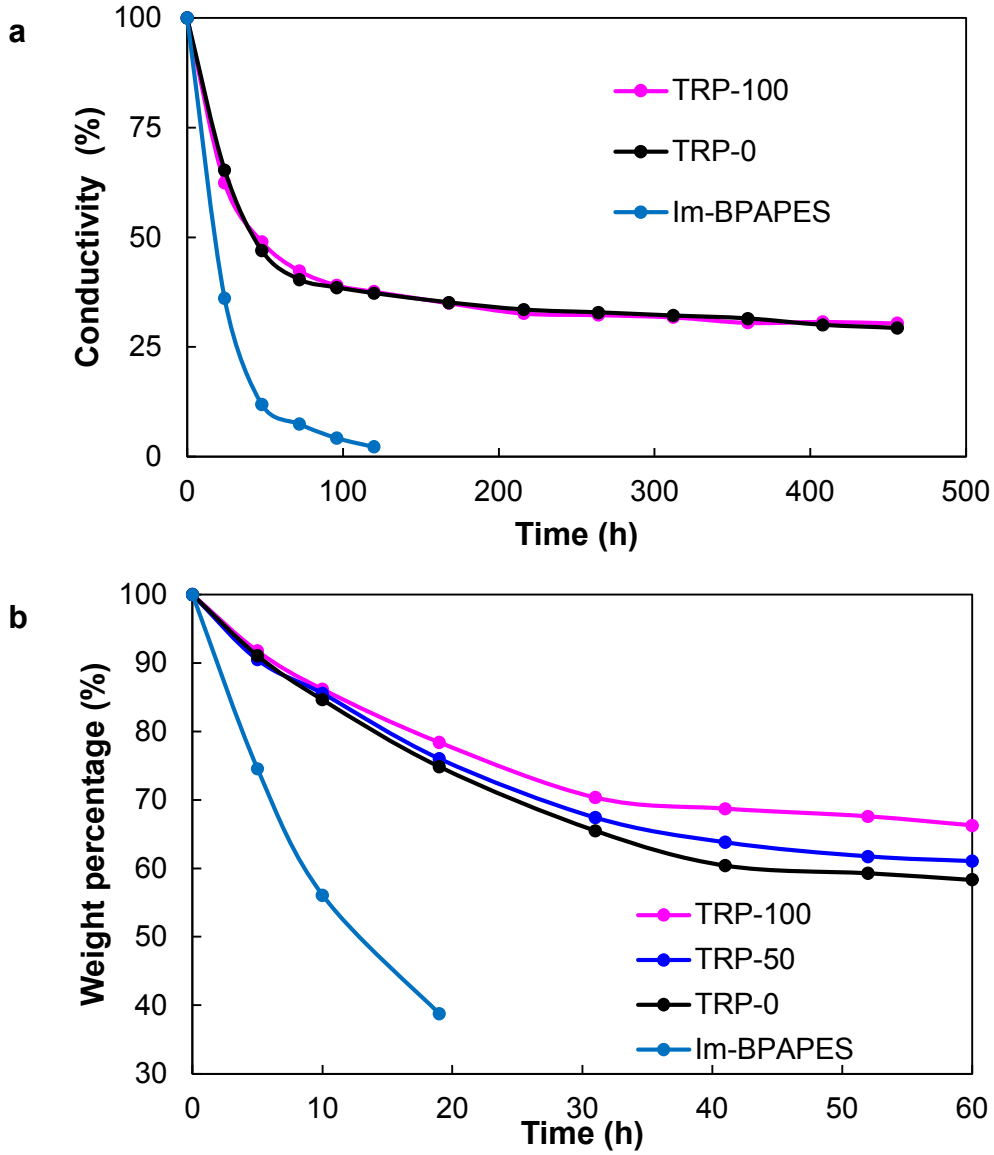


Figure 4. Time dependent hydroxide ion conductivity of the samples. Samples were soaked in 1 M NaOH at 80 °C. Initial IEC for TRP-0 and TRP-100 were 2.40 mmol/g, and Im-BPAPES was 1.83 mmol/g. b, Time dependent oxidative stability of the samples. Samples were soaked in 3% H_2O_2/4 ppm Fe^{2+} solution at 80 °C.

The membranes were soaked in a 1 M NaOH solution at 60 °C to evaluate their alkaline stability. After treating the membranes for the required amount of time, the membranes were washed and soaked in degassed deionized water and the time dependence of the ionic conductivity was determined (Figure 4a). Conductivity of highly functionalized additive-free Im-

BPAPES (IEC = 2.40 mmol/g) decreases rapidly. In addition, these membranes disintegrated as a result of excessive swelling after 120 h, making further measurements unreliable. With additives, an initial sharp decrease in conductivity within the first 72 h was observed as well. However, the conductivity stabilized to a constant value to retain ca. 30% of the original values: 0.0054 S/cm and 0.009 S/cm for TRP-0 and TRP-100, respectively. With more stable cationic groups such as substituted imidazoliums, we are hopeful that the improvements in stability resulting from the additives can be further enhanced and sustained.[31]

Oxidative stability of the membranes is crucial as long living superoxide anion radicals ($O_2^{\bullet-}$) are often generated under the harsh operating conditions of alkaline fuel cells. $O_2^{\bullet-}$ generated could attack the ether linkages and eventually lead to disintegration of the backbones.[32,33] Thus, membrane stability in strong oxidative condition was simulated by soaking the membrane in Fenton's reagent at an elevated temperature of 80 °C (Figure 4b). Similar to the trend of hydroxide ion conductivity in NaOH solution, weight of Im-BPAPES decreases rapidly within the first 20 hours to the point that the membrane was no longer measureable. On the other hand, masses of membranes with additives decreases gradually and stabilized after 40 h retaining ca. 60 %, 64 % and 69 % of the initial weight of TRP-0, TRP-50 and TRP-100, respectively. Hydroxide conductivity of TRP-100 at 30 °C after the oxidative stability test for 60 h decreased from 0.031 S/cm to 0.012 S/cm, suggesting a loss of functional groups within the membrane. However, the membrane retained fairly high amount of its conductivity, suggesting that the membrane was stable after the initial mass loss.

Addition of free volume promoting triptycene polymers into the anion exchange membranes enhances a number of performance metrics, including higher ionic conductivity,

improved mechanical and chemical stability. The higher ionic conductivity was attributed to additive promoted nanoscale hydrophobic/hydrophilic phase separation. Enhanced mechanical properties are consistent with the triptycene molecules that promote interlocking rigidifying interactions between polymer chains. Further studies using other free-volume promoting molecular building blocks combined with effective strategies for nanoscale phase separation are in order. Our expectation is that these and related strategies will contribute to the development of new generations of high performance anion exchange membranes for electrochemical conversion and storage devices, such as redox-flow batteries, electrodialysis, and high power output fuel cells.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. ‡These authors contributed equally.

Notes

There are no conflicts to declare.

Supporting Information

Details about materials, synthetic protocols and characterization methods supplied as Supporting Information.

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Graphic for manuscript