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Cross-linked comb-shaped anion exchange membranes with high base stability;

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A unique one-step cross-linking strategy that connects quaternary ammonium centers using Grubbs II-catalyzed olefin metathesis was developed. The cross-linked anion exchange membranes showed swelling ratios of less than 10% and hydroxide conductivities of 18 to 40 mS cm⁻¹. Cross-linking improved the membranes' stability to hydroxide degradation compared to their non-cross-linked analogues.

The design of new, highly anion-conducting polymeric materials has been the subject of intense research because of anion exchange membranes' potential application in fuel cells, electrolysis devices, water treatment technology, and other important technological areas.¹ Among them, anion exchange membrane fuel cells (AMFCs) have received significant interest in recent years relative to acidic fuel cells, because of alkaline fuel cells' significant advantages of improved oxygen reduction kinetics and better fuel oxidation kinetics at high pH which can lead to higher cell efficiencies and enable the use of non-precious metal catalysts, greatly reducing the cost of electrochemical devices.² As a critical component of AMFCs, the ionic conductivity and chemical stability of the anion exchange membrane controls the performance and lifetime of the device. The ionic conductivity of a polymer is related to a combination of its ion exchange capacity (IEC), the hydration level, and the microphase separated morphology of the material.³ Generally, high IEC values induce high ionic conductivity, but unfortunately increasing the IEC is accompanied by a significant increase in water uptake which can lead to uncontrolled dimensional swelling, loss of mechanical properties,^{2a,c} or even disintegration of the AEM, especially at elevated temperatures. For example, uncross-linked quaternary phosphonium poly(arylene ether sulfone)⁵ having an IEC value of ~ 1.2 meq. g⁻¹ showed an excessive swelling ratio of more than 100% at 60 $^{\circ}$ C.

Covalent cross-linking has been reported as an effective method to stabilize AEMs against high water swelling. Multifunctional groups

incorporating cross-linkable moieties, for example, dithiol,^{4a} dialdehyde,4b tri/tetraalkoxysilanes,4c and tetraepoxy4d have been widely used for AEM cross-linking. Thermal Friedel-Crafts electrophilic substitution-based cross-linking has also been developed to reduce swelling and methanol permeability,5 and a simultaneous polymerization and cross-linking technique using ring-opening metathesis polymerization at mild reactive conditions was reported to prepare high-performance AEMs.⁶ However, these cross-linking strategies usually require the introduction of an additional crosslinkable molecule or the method is based on thermal cross-linking (high temperature), which increases the process complexity and can adversely degrade the cationic groups. Cross-linking of quaternary ammonium-based polymers using commercial diamines (for example N, N, N', N'-tetramethyl-1,6-hexanediamine, TMHDA) has been developed as a promising cross-linking technique for high performance ionomers or membranes for alkaline fuel cells.⁷ However, working with diamines is not necessarily desirable in the preparation of samples and the polymer becomes insoluble after cross-linking, which is not compatible with the practical fabrication of electrochemical devices. Additionally, the alkaline stability enhancements afforded by this approach are still a major challenge in the development of cross-linked AEM because the functional groups based on commercial diamines are easily degraded by hydroxide through Hoffmann elimination.^{2a,7}

A polymer solution with a low-boiling point water-miscible solvent is required for the preparation of polymer-impregnated porous electrodes in order to maximize the catalyst/electrolyte interface and fabricate robust devices.⁸ Therefore, ionomers possessing high ionic conductivity and dimensional stability, as well as the ability of being used as both solutions and cross-linked membranes, are required for practical use in alkaline fuel cells.

In this work, we report a unique one-step cross-linking strategy to directly connect the quaternary ammonium groups on a poly-(2,6-dimethyl-phenylene oxide) (PPO) backbone using a high efficiency olefin metathesis technique that does not require heating or a separate crosslinker molecule aside from addition of Grubbs II catalyst (3.5 wt%). The AEM system we have been studying is combshaped quaternized PPO with one alkyl side chain, which possesses

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Scheme 1 Synthesis of cross-linked comb-shaped AEMs, XxYy, with one alkyl side chain using olefin metathesis with Grubbs II catalyst.

high stability of the cationic functional groups and excellent solubility in low-boiling point water-miscible solvents before cross-linking.⁹ For cross-linking by olefin metathesis, N,N'-dimethyl-10-undecen-1amine was prepared in high yield. The purity and chemical structure of the alkene-containing amine was confirmed by ¹H NMR spectroscopy (Fig. S1, ESI⁺). Preparation of the cross-linkable comb-shaped ionomers, XxYy, were achieved by the Menshutkin reaction of the olefinic amine with exclusively bromomethylated PPO which was prepared according to previous literature,9 as shown in Scheme 1 and Scheme S1 (ESI^{\dagger}) (where the x are the degree of bromination of PPO; y refer to the degree of cross-linkable alkene groups). Olefin metathesis with Grubbs II catalyst showed slow reaction at room temperature in dilute solution, but formed cross-links during membrane casting and drying.⁶ Thus, the alkene-functionalized PPO could remain soluble in solution (n-propanol and toluene mixtures) and then be cross-linked upon solidification at room temperature to obtain cross-linked XxYy membranes. Unlike previously reported cross-linking in which the degree of cross-linking was difficult to quantify,⁵ the Grubbs-catalyzed cross-linking appears to be controllable according to the amount of alkene groups in the polymer.

The degree of bromomethylation in this paper was designed to be 60% and 80%, and the concentration of cross-linkable groups was in the range of 25-100% which was further confirmed by ¹H NMR as shown in Fig. S2 (ESI⁺). Before cross-linking, these high IEC copolymers were not able to form transparent and flexible membranes due to their water solubility and immiscibility between the long alkyl chain and PPO backbone.9 However, tough and flexible membranes were achieved readily by Grubbs II-catalyzed olefin metathesis cross-linking. The IEC value of the obtained membranes ranged from 2.42 to 3.20 meq. g^{-1} by titration, which agreed well with the values calculated from ¹H NMR analysis. The cross-linked membranes could not be dissolved in water, methanol or n-propanol suggesting high degrees of cross-linking. Moreover, the olefin metathesis cross-linking drastically lowered the water uptake and thus the swelling ratio of the materials (Table 1). Specifically, the cross-linked X80Y40 sample had a water uptake of 29% and swelling ratio of 5.4% at room temperature, which is significantly improved compared to the uncross-linked X80Y40 that dissolved in water. At high temperature (80 °C), the cross-linked XxYy membranes retained their excellent dimensional stability with equal to or less than 10% swelling ratio, even at lower degrees of cross-linking (Fig. 1a). Considering the remarkable agreement

Table 1 Properties of cross-linked, comb-shaped XxYy membranes

Sample	$\frac{\text{IEC}^a}{(\text{meq. g}^{-1})}$	WU^b (%)	SR ^c (%)	σ^d (OH ⁻)	$\frac{\mathrm{SR}_{\sigma}^{e}}{(\% \mathrm{ cm m S}^{-1})}$	σ^d (HCO ₃ ⁻)
X60Y15	2.76	31	6	28	0.21	7.3
X60Y30	2.63	22	4	25	0.16	6.1
X60Y60	2.42	18	3	18	0.17	4.5
X80Y20	3.20	38	8	40	0.20	9.6
X80Y40	3.04	29	6	36	0.16	7.8
X80Y80	2.75	22	4	19	0.21	5.0
CL-TQPQ ⁵	1.23	_	15	38	_	_
QAPSU ^{10c}	2.31	41	17	40	_	_
FAA ⁵	1.60	—	26	17	_	_





Fig. 1 (a) Water swelling ratio as a function of degree of cross-linking at 20 °C and 80 °C; (b) hydroxide conductivity of **XxYy** and literature values for reported AEMs¹⁰ (circles) (uncross-linked QAPSU,^{10c} FAA⁵ and cross-linked CL-TQPQ⁵ membranes) as a function of water swelling ratio.

between the high solvent resistance and low swelling ratio, a strong covalent cross-linking network was likely formed by the Grubbscatalyzed cross-linking which was further confirmed by the gel fraction in NMP (> 80%) (Table S1, ESI†).

Fig. 2 shows the small-angle X-ray scattering (SAXS) profiles of the dry membranes, which displayed a clear peak for all cross-linked comb-shaped PPOs. This data is indicative of nanophase separation between the hydrophilic quaternized PPO backbone and the hydrophobic alkyl side chains leading to a periodic structure at a length



Fig. 2 Small angle X-ray scattering (SAXS) of dry comb-shaped **XxYy** and membranes in bicarbonate form.

scale of $d = 2\pi/q_{\text{max}}$, where q_{max} is the peak maximum.¹¹ The corresponding d-spacing values fall into the range of 1.7-2.5 nm $(2.5-3.6 \text{ nm}^{-1})$, which roughly correspond to the length of the extended aliphatic side chains. An ordered morphology was observed in the case of the lightly cross-linked X60Y15 sample which did not show any order in its uncross-linked form, Fig. 2. We hypothesize that the cross-linking induced order in the X60Y15 sample by coalescing domains of alkyl chains due to the metathesis linking of the terminal alkenes. The ionic domain peak of the highly cross-linked membrane X60Y60 shifted to higher q (lower d spacing) upon cross-linking likely indicating compression of the ionic domains or further exclusion of other moieties with cross-linking, although the cross-linked X60Y60 peak breadth did increase slightly. The relatively large width of the peaks indicates a weak separation between the two components, and the fact that that no second order peak was observed suggests that the arrangement of the phase separated domains was only locally correlated and no long-range ordered structures were formed.

The phase-separated, cross-linked membranes exhibited hydroxide conductivities of 18–40 mS cm⁻¹ at 20 $^{\circ}$ C which was much greater than the conductivities of typical PPO AEMs based on trimethylamine (IEC = 1.39 meq. g⁻¹, OH⁻ conductivity: 5 mS cm⁻¹), and meets the basic requirement for membranes in AMFCs $(>10^{-2} \text{ S cm}^{-1})$.⁹ If bicarbonate species should form in the membrane under operating conditions,¹² the conductivities of our system are still comparable to other cross-linking-free comb-shaped AEMs.9 The cross-linked comb-shaped membranes showed a much lower swelling ratio (<10%) but comparable conductivity to those reported for quaternary ammonium AEMs in the hydroxide form. Specifically, quaternary ammonium poly(sulfone) (QAPSU) AEMs reported by Zhang^{10c} and co-workers exhibited a swelling ratio of 17% and OH^- conductivity of 40 mS cm⁻¹ at 20 °C, a commercial FAA-QAOH sample had a swelling ratio of 26% and hydroxide conductivity 17 mS cm⁻¹, and a cross-linked quaternary phosphonium (CL-TQPQOH, IEC = 1.23 meq. g^{-1}) AEM possessed a swelling ratio of 15% and OH⁻ conductivity of 38 mS cm⁻¹ reported by Yan, et al.⁸ Overall, the cross-linked XxYy membranes showed higher hydroxide conductivity but lower swelling ratios than these samples, as shown in Fig. 1b. To quantitatively describe the trade-off behaviour between swelling and conductivity, the hydroxide conductivity-normalized swelling ratio was calculated (SR₅, Table 1). Generally, a high membrane swelling ratio at a given IEC value will dilute the concentration of ionic charges, and thus decrease the ionic transport within the membrane. Having reduced membrane swelling and good hydroxide conductivity, the X60Y15 sample had the lowest hydroxide conductivity-normalized swelling ratio $(0.16-0.21\% \text{ cm mS}^{-1})$ reported, which is much lower than other cross-linked or noncross-linked AEMs (0.47-3.85% cm mS⁻¹).13 These results suggest that our olefin metathesis cross-linking concept mitigates AEM swelling and could increase the concentration of charge carriers in the sample and thus maintain ion conductivity.

In addition to the excellent dimensional stability and high ionic conductivity of these materials, cross-linked comb-shaped membranes displayed good alkaline stability which is critical for AMFC operation. The **XxYy** membranes remained intact, transparent, and flexible after immersion in 1 M NaOH (pH \sim 14) at 80 °C

for 30 days, while under similar conditions the typical benzyl trimethyl quaternary ammonium-based PPO membranes became very brittle due to severe degradation. Additionally, non-cross-linked, comb-shaped membranes became opaque under these degradation conditions.⁹ No significant loss in conductivity or IEC for XxYy AEMs were observed after alkaline stability testing, which supports their excellent long-term stability, as shown in Fig. S3 and S4 (ESI⁺). Unlike the previously reported TMHDA cross-linked AEMs, in which the β-hydrogens of the quaternary ammonium pendant alkyl chains induced the rapid degradation of quaternary ammonium groups by Hoffmann elimination, the longer alkyl side chain protected the QA groups from degradation by hydroxide. Moreover, improved alkaline stability was observed for all cross-linked XxYy AEMs compared to non-cross-linked AEMs with one long alkyl side chain (Fig. S3 and S4, ESI⁺), likely due to the steric hindrance of the coupled, longer alkyl chains after cross-linking.14

In summary, we have designed and demonstrated a new class of cross-linkable, comb-shaped cationic copolymers for stable anion exchange membranes. The cross-linked AEMs were achieved by Grubbs-catalyzed olefin metathesis and the degree of cross-linking could be controlled readily by tuning the amount of alkene groups pendant to the polymer chain. Outstanding dimensional stability, even at high temperature (80 °C) was observed for all cross-linked AEMs. The cross-linked AEMs exhibited nanoscale organized phaseseparated morphology, resulting in high ion conductivity compared to typical PPO AEMs containing benzyltrimethyl ammonium cationic groups. In addition, the cross-linking of alkyl side chains improved the alkaline stability of the AEMs relative to the non-cross-linked AEMs. After 30 days immersion in 1 M NaOH at 80 °C, no obvious changes in IEC and conductivity were observed. The combination of excellent solubility of the precursor polymer in low-boiling-point solvents makes the olefin metathesis cross-linking of comb-shaped copolymers attractive as a method for producing high-performance AEM materials for fuel cell applications.

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