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Toward High Conductivity in Anion Exchange Membranes for Alkaline Fuel Cells Application

Nanwen Li,^{*,[a]} Michael D. Guiver,^[b] Wolfgang H. Binder^{*,[a]}

Quaternized poly(2,6-dimethylphenylene oxide)s (PPOs) having clicked 1,2,3-triazole were first prepared by Cu(I) catalyzed 'click chemistry' for improving the anion transport in anion exchange membrane (AEM). Clicked 1,2,3-triazoles incorporated into AEMs provide more sites to form efficient continuous hydrogen-bond networks between water/hydroxide and triazole for anion transport. Higher water uptake was observed for these triazole membranes. Thus, the membranes showed an impressive enhancement of hydroxide diffusion coefficient and thus the anion conductivities. The recorded hydroxide conductivity was 27.8–62 mS/cm at 20 °C in water, which was several times higher than that of typical PPO-based AEM (TMA-20) derived from the trimethylamines (5 mS/cm).

Even at reduced relative humidity, the clicked membrane also showed superior conductivity to a trimethylamine based membrane. Moreover, similar alkaline stabilities at 80 °C in 1 M NaOH were observed for the clicked and non-clicked membranes. The performance of a H₂/O₂ single cell assembled with clicked AEM is much better than that of a non-"clicked" TMA-20 membrane. The peak power density achieved for AFC with the **1a**(20) membrane was 188.7 mW cm⁻² at 50 °C. These results indicate that clicked AEM could be a viable strategy in improving the performance of alkaline fuel cells.

Introduction

There have been intensive research efforts directed toward the development of anion exchange membranes (AEMs) for solid state alkaline fuel cells (AFCs) and water electrolyzers in recent years.^[1] These devices permit the use of non-platinum-group metal electrocatalysts for the oxygen reduction/evolution and hydrogen oxidation/evolution reactions.^[2] In fuel cells, the electrolyte (i.e., AEM) materials have two primary functions - as selective ion transport media (ion conductor) and electric insulators (separator) between two electrodes. Besides their use in AFCs, AEMs are highly relevant for other electrochemical energy conversion/storage devices such as redox flow batteries, electrodialysis stacks, and metal-air batteries.^[2c] The renewed interest in AFCs has led to many studies directed toward improving the hydroxide ion conductivity of AEMs, a property that is inherently limited by the lower intrinsic mobility of the hydroxide ion. Indeed, it has been a scientific challenge to develop an inexpensive polymer that can achieve a balanced set of properties with high conductivity, acceptable water swelling, and long term chemical stability under severe electrochemical conditions. Various synthetic strategies have been explored to improve conductivity, such as changes in the basicity^[3] and the position of quaternary ammonium groups,^[3c,4] crosslinking,^[5] and the control of membrane morphologies by block copolymer architectures,^[6] but these approaches have achieved only limited success. Therefore, increasing the ionic conductivity of

AEMs to achieve higher operation efficiencies remains a significant challenge and is currently an area of intense research.

It was assumed that the hydroxide transport mechanisms in the AEMs could be analogous to that of the transport of protons in proton exchange membranes (PEMs), e.g. the *vehicle mechanism* and the *Grøtthuss-type mechanism*.^[7] The *vehicle mechanism* occurs by the formation of an ion adduct composed of an ion and a diffusible carrier molecule,^[7b] while the *Grøtthuss-type mechanism* involves the transport of ions from site to site without a carrier molecule, where its activation energy depends on the hydrogen bond breaking energy and the distance between the interacting sites.^[7c] In the case of hydroxide transport through AEMs, a *Grøtthuss-type mechanism* was considered to be the dominant transport mechanism based on the fact that hydroxide exhibits *Grøtthuss* behavior in aqueous solutions, comparable to protons.^[8] However, there are fundamental discrepancies between PEM and AEM conductivities, in spite of the comparable mass diffusion coefficients of hydroxides and protons^[9b] and the same dominant transport mechanisms through the membrane. Several researchers^[8a,9] have proposed that the hydronium ions are naturally integrated into the hydrogen-bonding network of water, whereas hydroxide ions tend to have stable solvation shells that reorganize the solvent molecules and perturb the hydrogen bond network.

The main purpose of this paper is to focus on alternative hydroxide transport facilitators that form efficient hydrogen bonded networks. Heterocycles, such as imidazole containing polymers, were studied as hydroxide ions solvent (doped with KOH) in AEMs for AFCs.^[10] Unfortunately, the conductivity and thus AFC performance drops rapidly with the loss of basic dopants, especially when exposed to water. 1,2,3-Triazoles, which can lose a proton to act as a weak acid or accept a proton using the lone pair electrons located on its nitrogen atoms as a weak Brønsted base^[11] have been investigated recently in PEMs to promote proton transport through inter- or intramolecular proton transfer for high temperature fuel cells.^[12]

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However, we are not aware of any reports of triazoles being used as a conductor for hydroxide ion transport in AEMs. The expectation of choosing triazoles is that the barrier for hopping of hydroxides among various sites either intra- or intermolecularly will be low as a consequence of the high density of sites available for residence at a shallow potential-energy distribution among these sites. Moreover, the triazole groups are expected to form a dense, continuous 3D network of hydrogen bonds with hydroxide and water, which would be favorable to create a matrix for hydroxide diffusion.

Among the potential triazole species, the clicked 1,2,3-triazole (Scheme 1) was selected because it can be prepared readily *via* Cu(I)-catalyzed 'click chemistry' (CuAAC), which is a well-known method for linking reaction partners in high efficiency under moderate reaction conditions, and is largely solvent insensitive.^[13] Moreover, the hydroxide conductive quaternary ammonium (QA) groups can also be introduced simultaneously into the polymer backbone to obtain AEMs (without basic dopants) having a 'side-chain-type' structure, which has been claimed to improve the hydroxide conductivity.^[3c,4b-c]

Results and Discussion

Polymer Synthesis and Characterization

The synthesis of such AEMs used in this study involves the combination of an alkyne-functionalized quaternary ammonium (Scheme S1) and an azide-modified polymer backbone (Scheme S2). The alkyne-functionalized quaternary ammonium-compound based on trimethyl amine was synthesized in one straightforward, high-yielding step. The chemical structures were further confirmed by ¹H NMR as shown in Figure S1. Poly(2,6-dimethyl-phenylene oxide) (PPO) with molecular weight of 20,000 was selected due to its commercial availability and amenability for modification. The methyl-brominated PPO (PPO-Br) having different degrees of substitution (DS) (*x*) were obtained according to our previous reported procedures (see Supporting Information).^[14] The azidation-reaction was carried out with the use of NaN₃ in DMF for 24 h at 80 °C. As shown in Figure 1, the chemical shift corresponding to benzylic methylene shifted from 4.42 ppm to 4.14 ppm indicating successful azidation. The functionalization with the azide was further proved by the appearance of the characteristic peak of azide groups around 2120 cm⁻¹ in FT-IR spectroscopy, as shown in Figure S2. After treatment with sodium azide, the obtained azide-modified PPOs (PPO-N₃) were further functionalized with clicked QA groups by Cu(I)-catalyzed alkyne-azide 'click chemistry' to obtain the copolymers **la**(*x*) (where the *x* refers to the degree of substitution), as shown in Scheme 1.

Scheme 1. The synthesis of clicked copolymers **la**(*x*) and **lb**(*x*) by Cu(I)-catalyzed alkyne-azide 'click chemistry' (CuAAC).

When probing several ligand/Cu(I)-catalyst-combinations (CuBr) to promote the formation of the Cu(I)-acetylide,^[13a] N,N,N',N''-pentamethylethylenetetramine (PMDETA) in combination with Cu(I)-CuBr emerged as the most reactive "click"-system, enabling the functionalization of PPO-N₃ quantitatively at 50 °C for 10 hours. As proven by NMR-spectroscopy the methylene protons were completely shifted from 4.23 to 5.62 ppm while the aromatic proton remained intact (Figure 1). The appearance of the proton in 1,2,3-triazole at 8.43 ppm and the additional peaks of the methylene protons linked to the QA unit at 4.62 ppm further proved the successful 'click' reaction. Additionally, the band of 2120 cm⁻¹ for azide groups in FT-IR spectroscopy disappeared completely in clicked copolymers after successful 'click' functionalization (Figure S2). GPC analysis of **la** shown in Table S1 revealed no obvious decomposition of polymer backbone was found during the functionalization process. The ion-exchange capacities (IEC) of **la** were determined to be in the range of 0.99 to 1.80 meq. g⁻¹, calculated from the integral ratio of aromatic protons (H1, H3) to H8, which was in good agreement with the calculated value from the copolymer composition (Table S2). Transparent and flexible brown colored membranes were cast from NMP solutions in the bromine form.

Figure 1. The ¹H NMR spectra of PPO-Br(20), PPO-N₃(20) in CDCl₃ and **la**(20) copolymers in DMSO-*d*₆.

Water Uptake of Membranes

The ion exchange capacities (IEC) values correlated with the water uptake (WU) for **la** membranes (Table 1) as expected. Water uptake of the **la** membranes, which was in the range of 22.4 to 39.8 % at 20 °C, increased linearly with increasing IEC, as shown in Figure 2a. For a better comparison among the different IEC membranes, the number of absorbed water molecules per quaternary ammonium (QA) group (designated as λ) was calculated. A higher λ value was observed for

clicked **la** membranes ($\lambda \sim 12$) compared with PPO bearing benzylic tetramethyl ammonium membrane (TMA-20) (IEC = 1.39 meq. g⁻¹; $\lambda \sim 10$), as shown in Table 1. These higher water uptake values for **la** membranes suggest that the triazole groups provide more sites for water and/or hydroxide to form more effective and continuous hydrogen-bonding networks (as discussed below).

Table 1. Properties of la (x), lb (30) and TMA-20 membranes.						
samples	IEC ^a	WU (wt %) ^b	λ	σ (OH ⁻) ^b	σ (HCO ₃ ⁻) ^b	σ (CO ₃ ²⁻) ^b
la (14)	0.99	22.4	12.6	27.8	7.3	12.6
la (20)	1.32	29.2	12.3	43.4	10.2	20.5
la (30)	1.80	39.8	12.3	62.0	16.7	31.2
lb (30)	1.50	32.0	11.8	32.0	9.1	15.2
TMA-20	1.39	25.9	10.4	5.0	1.4	2.4

[a] Calculated from ¹H NMR; [b] measured in water at RT (mS cm⁻¹).

In addition, the volumetric IEC value of water absorbed membranes (IEC_v (wet)), calculated from density and water uptake measurements, reflects the concentration of ions within the polymer matrix under hydrated conditions without distinguishing between those hydroxides that are mostly associated with the QA groups and those that are fully dissociated. It is of interest to note how this IEC_v (wet) value itself is affected by changes in base and water uptake and whether ion concentration remains constant or whether it varies. As shown in Table 2, the IEC_v of **la** membranes at 20 °C increased from 0.82 to 1.32 meq./cm³, corresponding to IEC values increasing from 0.99 to 1.80 meq./g.

Figure 2. a) Water uptake and b) IEC-normalized hydroxide conductivity of **la**(x) and TMA-20 membranes at 20 °C as a function of IEC.

Anion Conductivities of Membranes

The hydroxide conductivity of the **I** membranes was measured in water and compared to that of TMA-20 based on typical trimethylamine AEMs. Remarkable hydroxide conductivities of **la** membranes are observed. For example, **la**(20) membrane displayed hydroxide conductivity of 43.4 mS cm⁻¹ at room temperature (measured by the four-point probe in-plane

method due to its greater reproducibility) under a fully hydrated state, which is almost ten times that of a TMA-20 membrane with similar IEC value and water uptake, demonstrating the excellent conductivity and scope of this system. The highest hydroxide conductivity of 62 mS cm⁻¹ at 20 °C was achieved for the **la**(30) membrane with an IEC value of 1.80 meq. g⁻¹. By comparison, Varcoe and Slade AEMs exhibited 34 mS cm⁻¹ at 50 °C for the hydroxide form.^[15a] Cornelius and co-workers^[15b] observed conductivities of 50 mS cm⁻¹ at 30 °C for a poly(phenylene)-based system, and another system by Zhang^[15c] et al. showed 40 mS cm⁻¹ at 20 °C. More importantly, the **la**-membranes exhibit a much higher IEC-normalized hydroxide conductivity (28.1–34.4 mS g cm⁻¹ meq.⁻¹) than that of TMA-20 membrane (3.6 mS g cm⁻¹ meq.⁻¹), as shown in Figure 2b.

Figure 3. (a) Hydroxide diffusion coefficient of **la**(x) and TMA-20 membranes as a function of volumetric IEC_v in the water at room temperature; (b) humidity dependence of hydroxide conductivity for the **la**(20) and TMA-20 membranes at 50 °C.

As a hypothesis, we assumed that the triazole groups provide continuous sites for hydrogen bonds that can likely promote long-range hydroxide transport in the polymer system by *Grotthuss-type mechanism*, thus the increased ion conductivities. As the morphological structures of **la**(20) and TMA-20 revealed a similar disordered microphase, no obvious ionic clusters peak were observed via small angle X-ray scattering (SAXS), Figure S3. To further confirm this hypothesis, pulsed magnetic field gradient (PMF) NMR spectroscopy was used to study the self-diffusion coefficient of water in AEMs.^[16] As shown in Figure S4, the **la** membranes displayed lower water diffusion coefficients (0.8×10^{-10} – 2.3×10^{-10} m² s⁻¹) in comparison to the TMA-20 membrane (3.2×10^{-10} m² s⁻¹), suggesting that the water moves more slowly in **la** membranes and is more closely bound by stronger interactions between water and polymer than it is in the TMA-20 polymer. If the density of **la**(14) (1.01 g cm⁻³) and TMA-20 (1.03 g cm⁻³) are taken into account, sample **la**(14) displayed a much lower volumetric IEC value (IEC_v) (0.82 meq cm⁻³) which reflects the concentration of ions within the polymer matrix under hydrated conditions without distinguishing between those hydroxides that are mostly associated with the quaternary ammonium groups and those that are fully dissociated than that of TMA-20 (1.13 meq cm⁻³). Therefore, combined with the similar

morphological structures, it can be concluded that an attractive interaction between triazole groups and water and/or hydroxide makes the major contribution to the enhanced hydroxide conduction.

To further elucidate the hydroxide-conducting properties of the **la** membranes, the effective hydroxide diffusion coefficients (D_o) through the membranes were estimated from the hydroxide conductivity and the IEC_v in hydrated membranes when a relatively complete dissociation of hydroxide may be assumed for all the membranes. As shown in Figure 3a, the hydroxide diffusion coefficients of **la** membranes ($9.02\text{--}12.5 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$) are much higher when compared to TMA-20 ($1.2 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$), in spite of their lower volumetric IEC_v . These results are consistent with the fact that the **la** membranes having lower IEC_v showed higher hydroxide conductivities. As discussed above, the higher D_o values are likely attributable to interaction between triazole groups and water and/or hydroxide which provide more sites for hydroxide and/or water transport in AEMs and thus the conductivity. In addition, higher hydroxide conductivities at reduced relative humidity (RH) and lower RH dependence of conductivity for the clicked **la**(20) membranes were observed compared with TMA-20 (Figure 3b), which further confirms that the increased number of hydrogen bonds forming and breaking sites (triazole) combined with the shorter distance between them leads to an effective hydroxide transport in clicked AEM.

Figure 4. a) Decline in conductivity of AEMs during conductivity measurements expose to atmosphere air at room temperature; b) Impact of temperature on the conductivity for the AEMs in the HCO_3^- form.

If carbonate and bicarbonate species should form in the membrane under operating conditions, the conductivities of our system are still significant, as shown in Table 1. Indeed, it has even been shown that power densities can be as good or better when CO_2 is introduced into an AFC due to improved electrode kinetics in the presence of carbonate.^[17] Figure 4a illustrates the correlation between conductivity and testing time for **la** and TMA-20 membranes when the testing cell was exposed to ambient air. All AEMs had a decline in ionic conductivity over several tens of hours (Figure 4a), since the OH^- in AEMs was probably neutralized by the absorbed CO_2 from ambient air.^[17] However, a lower rate of decline was observed for **la** membranes, which is assumed to be due to the

hydrogen bonding network weakening the ability of CO_2 absorption. Higher degradation temperature of QA was observed for the **la** membrane than that of the TMA-20 membrane (Figure S5), further suggesting the existence of interactions between the triazole and the hydroxide ions. Interestingly, after 4 days of exposure of the membrane in water to ambient air, the conductivity of the samples was the same as for samples purposely ion exchanged to the bicarbonate form. It is believed that the bicarbonate form of the membrane is formed first when the CO_2 was absorbed. The correlation between HCO_3^- conductivity and temperature for **la** and TMA-20 membranes is shown in Figure 4b. The conductivity steadily increases with temperature and exhibits the highest conductivity of 34 mS cm^{-1} for a **la**(30) membrane at 80°C . At 50°C the HCO_3^- conductivity of **la**(30) having a WU of 32.5 % was 23.3 mS cm^{-1} which is comparable to the previous reported values ($10.1\text{--}25.7 \text{ mS cm}^{-1}$) for high WU AEMs (WU > 50 %).^[4a,5b,18]

Table 2. The in-plane and through-plane bicarbonate conductivities of clicked **la**(x) and TMA-20 membranes measured by the two-point probe method at room temperature in water.

sample	IEC (meq./g)	IEC_v (meq./cm ³)	$\sigma_{\perp}$ (mS/cm)	$\sigma_{\parallel}$ (mS/cm)	$\sigma_{\perp}/\sigma_{\parallel}$
la (14)	0.99	0.82	5.5	6.5	0.85
la (20)	1.32	1.04	9.8	11	0.89
la (30)	1.80	1.32	12.4	14.8	0.84
TMA-20	1.39	1.13	1.9	2.1	0.9

To examine the anisotropic nature of conductivity, *through-plane* and *in-plane* bicarbonate conductivity values were measured for the clicked and non-clicked membranes by a two-point probe (Table 2). All the membranes were found to possess similar in-plane ($\sigma_{\parallel}$) and through-plane ($\sigma_{\perp}$) bicarbonate conductivities with the $\sigma_{\perp}/\sigma_{\parallel}$ value in the range of 0.84 to 0.89, indicating a mild degree of anisotropy which could be attributed to their similar disordered micro-morphological structures, as shown in the SAXS results. Additionally, the similar hydroxide conductivities in in-plane and through-plane (Table S3) further confirmed the mild degree of anisotropy of the membranes.

Alkaline Stability of Membranes

The long-term stability of AEMs is generally of concern due to known degradation pathways for tetraalkylammonium ions under alkaline conditions^[2a] such as via β -hydrogen Hoffmann elimination, direct nucleophilic substitution at an α -carbon, or via nitrogen ylide formation. The stability of these AEMs at 80°C in 1 M NaOH was investigated by conductivity and changes in IEC values.

A similar decomposition behavior was observed for **la** and TMA-20 membranes. As shown in Figure 5a, the membrane hydroxide conductivity declined rapidly within several tens of hours to ~60% of the initial value, and mechanical degradation occurred after 100 h. However, after an initial period of transient behavior for several tens of hours, the IEC values estimated from the ^1H NMR showed a constant but slow decline (Figure 5b) to ~ 50 % of their initial value. The methyl

proton signals of the QA group became smaller, while the aromatic proton signals between 6.5–6.8 ppm and triazole protons at 8.33 ppm showed little change when compared with those of the pristine samples. This result revealed that the clicked 1,2,3-triazole ring exhibits excellent stability under alkaline conditions. Since no other signals assignable to new methyl or methylene protons were observed in Figure S6 and S7, the major degradation mode of **la** and TMA membranes in alkaline stability test is most likely to involve a direct nucleophilic substitution, that is, the elimination of a tertiary amine. These results suggest that the clicked AEMs showed similar alkaline stability with TMA membrane containing benzylic tetramethyl ammonium. At higher NaOH concentrations, the **la** and TMA membranes also displayed similar degradation behavior at 80 °C. As shown in Table S4, the IEC and hydroxide conductivity of membranes decreased and the gel-fraction increased due to possible crosslinking of benzyl alcohol which results from the degradation of quaternary ammonium by elimination of a tertiary amine,^[6b] especially at the highest NaOH concentration of 10 M. Further theoretical and experimental studies are needed to determine the degradation mechanism of AEMs.

Figure 5. The changing trend in (a) hydroxide conductivity and (b) IEC values of **la** and TMA-20 membranes after immersion in 1 M NaOH solution at 80 °C.

H₂/O₂ Fuel Cell Performance

Figure 6 compares the polarization curves of an H₂/O₂ AEMFC with clicked **la**(20) and a control TMA-20 as the electrolyte membrane. Both of the open circuit voltages (OCVs) are close to the theoretical value of about 1.1 V, indicating that the electrolyte membranes do not affect the OCVs significantly. The peak power density for AEMFC with the **la**(20) membrane was 188.7 mW cm⁻², which was much higher than that of with the control TMA-20 membrane (62.3 mW cm⁻²) under the same testing conditions, in spite of the similar IEC values. The data further suggest that the clicked **la**(20) membrane has better properties (higher ion conductivities and better fuel cell performance) than that of the AEM without triazole groups.

Figure 6. Polarization curves (open symbols) and power density curves (filled symbols) of **la**(20) and the control TMA-20 incorporated AEMFC. Test conditions: membrane-thickness of 50 μ m, cell temperature of 50 °C, catalyst loadings of 0.5 mg Pt cm⁻² (Pt/C) for both anode and cathode, gas flow rate of 0.2 L min⁻¹ for both H₂ and O₂.

Clicked AEM with Guanidinium Groups

Figure 7. Comparison of the conductivity and water uptake for **Ib**(30) with clicked guanidinium and TMA-20 membranes.

To further confirm the effect of clicked triazole on the conductivity of AEMs, clicked PPO with guanidinium **Ib**(20), which has been claimed as a superstrong organic base^[3b], was prepared by a synthetic process similar to that described above (Scheme 1). Herein, the butyl chain was introduced and expected to increase the volume which would possibly weaken the interaction between the water and/or hydroxide and triazole. The IEC of **Ib**(30) was determined to be 1.50 meq. g⁻¹ according to the ¹H NMR results. At room temperature, a **Ib**(30) membrane still absorbed more water and displayed 7 times higher hydroxide conductivity than that of a TMA-20 membrane in spite of the large volume of the butyl chain, as shown in Figure 7. The results suggest the existence of interactions between water or/and hydroxide and triazole rings and its promotion effects of hydroxide transport in AEMs. The higher hydroxide ion diffusion coefficients in the **Ib** membrane (8.1×10^{-9} cm² s⁻¹) compared to that of the TMA-20 membrane (1.2×10^{-9} cm² s⁻¹) further confirms such interactions. Meanwhile, high bicarbonate and carbonate conductivities

were also observed for the clicked **1b** membrane. From these results, it is clear that the incorporation of triazole invokes a significant improvement in ion-conducting behavior in the anion exchange membranes.

Conclusions

In summary, incorporation of clicked 1,2,3-triazole has been shown to effectively promote ionic conduction in anion exchange membranes. One possible reason is that the introduction of the 1,2,3-triazole results in hydrogen bonds forming a continuous pathway for ionic conduction and ion movement in a particular direction. The obtained membranes showed a significantly higher conductivity (up to 10 times) than that of the AEMs without triazole groups. The methodology is likely to be versatile as confirmed by the preparation of two AEMs with different QA groups. Further investigation into triazole and its derivatives, especially copolymers with stable QA groups, may be expected to have an impact in solid polymer electrolyte science, especially conductive membrane materials.

Experimental Section

Quarternization of the PPO-N₃ by 'click chemistry'

The copolymers were synthesized by click chemistry in NMP. In a typical experiment: To a 3-necked flask equipped with a magnetic stirring bar, PPO-N₃ (DS=0.3) (6 g, 50 mmol), PTMA bromide salts (3.5 g, 20 mmol), ligand (PMDETA, 10 mmol), catalyst (CuBr, 5 mmol) were dissolved in 5 mL of NMP. The flask was degassed by three freeze-pump-thaw cycles, left under vacuum, and placed in a thermostatted oil bath. The reaction was process at 50 °C for 12 h. The reaction mixture was then precipitated into water and then washed by water for three times. The as obtained clicked copolymer **1a**(30) (where x refers to the degree of bromination) was dried in vacuum at room temperature.

Membrane casting and ion exchange

The **1a**(x) copolymers in the bromine form were cast from NMP solutions (5 wt %) in a custom-built flat glass dish. The membranes were first dried at 80 °C for 12 h and then vacuum dried at 80 °C for 24 h. The membranes in the bicarbonate or carbonate form were achieved by exchanging the bromine form membranes with sodium bicarbonate or sodium carbonate followed by extensive rinsing to remove the excess salt. The membranes were treated in 1 N NaOH at room temperature for 24 h to obtain the hydroxide conductive **1a**(x) membranes. They were then washed thoroughly and immersed in deionized water that was degassed and blanketed with flowing Ar to remove residual NaOH.

Measurements

¹H NMR spectra were measured at 300 MHz on an AV 300 spectrometer using DMSO-*d*₆ or CDCl₃ as solvent. Ion exchange capacities (IEC) of the membranes were determined by ¹H NMR results. The thermogravimetric analyses (TGA) were obtained in nitrogen with a Perkin-Elmer TGA-2 thermogravimetric analyzer at a heating rate of 10 °C/min. The molecular weights of polymers were determined by gel permeation chromatography (GPC) using a Waters 515 HPLC pump, coupled with a Waters 410 differential refractometer detector and a Waters 996 photodiode array detector. THF or NMP was used as the eluant and the μ -Styragel columns were calibrated by polystyrene standards.

The density of the membranes was measured by a buoyancy method. Water uptake was measured after drying the membrane in hydroxide form at 60 °C under vacuum for 24 h. The dried membrane was immersed in water and periodically weighed on an analytical balance until a constant weight was obtained, giving the weight-based (IEC) water uptake. The volume-based IEC (IEC_v) was obtained by multiplying the membrane density by the IEC values which were estimated from the copolymer structure. This calculation resulted in IEC_v (dry) based on the dry membrane density. The IEC_v (meq./cm³) under wet form was then calculated based on membrane water uptake, using the following equation (1).

$$IEC_v = \frac{IEC}{\frac{1}{\rho_{polymer}} + \frac{WU \text{ (wt \%)}}{100 \times \rho_{water}}} \quad (1)$$

where IEC is the gravimetric IEC (meq./g) and ρ (g/cm³) is the density.

In plane conductivity (σ , Scm⁻¹) of each membrane (size: 1 cm × 4 cm) was obtained using $\sigma = d/L_s W_s R$ (d is the distance between reference electrodes, and L_s and W_s are the thickness and width of the membrane, respectively). The resistance value (R) was measured over the frequency range from 100 mHz to 100 kHz by four-point probe alternating current (ac) impedance spectroscopy, because the four-point in-plane method is the most common method due to its reproducibility, using an electrode system connected with an impedance/gain-phase analyzer (Solartron 1260) and an electrochemical interface (Solartron 1287, Farnborough Hampshire, ONR, UK). The hydroxide conductivity measurements under fully hydrated conditions in the longitudinal direction were carried out with the cell immersed in water which was degassed and blanketed with flowing Ar. Humidity during conductivity measurements was controlled using an Espec SH-241 (Osaka, Japan) humidity chamber. The oven temperature was maintained at 50 °C while relative humidity was varied from 30% to 95%.

For comparison, both of the in-plane and through-plane hydroxide conductivity ($\sigma_{||}$ and $\sigma_{\perp}$, respectively) of membranes was also determined using two-point probe method. For $\sigma_{||}$, a single cell with two plate electrodes was mounted on a Teflon plate at 1 cm distance. For $\sigma_{\perp}$, a membrane sample was sandwiched between two plate electrodes of 1 cm² area and mounted on two Teflon blocks. The cell was tightened with screws. The through-plane conductivity measurement was performed only on the cell placed in water, because the contact resistance between electrodes and membrane could be neglected only in the fully hydrated state. Through-plane

conductivity was also calculated using $\sigma = d/L_s W_s R$, except that d (cm) is the thickness of the membrane and $L_s W_s$ (cm²) is the area of the electrode. From the conductivity and density data, ion diffusion coefficients (D_o) were calculated using the Nernst-Einstein equation (2)

$$D_o = \frac{RT}{F^2} \frac{\sigma}{c(OH^-)} \quad (2)$$

where R is the gas constant, T is the absolute temperature (K), F is the Faraday constant, and $c(OH^-)$ is the concentration of hydroxide charge carrier (mol/L).

Small angle X-ray scattering measurements were performed on a SAXS setup using a Rigaku generator of rotating anode type with Cu target, equipped with a focusing multilayer optics. The flight path is fully evacuated, a 2D-Siemens Hi-Star served as detector. All the measurements were performed at room temperature. Typical exposure time was in the range from 20 min to 40 min, depending on the thickness of the sample. The samples were pressed to films at a temperature of about 25 °C and had a typical thickness about 0.1 mm. The accessible range of scattering vectors $q = 4\pi \sin\theta/\lambda$ was about 0.6 nm⁻¹ to 6.2 nm⁻¹. Here λ and 2θ are the X-ray wavelength and Bragg scattering angle, respectively.

Fuel cell performance evaluation

A well-dispersed catalyst ink was prepared by mixing 46.4 wt% Pt/C with de-ionized water, 1-propanol and 5 wt% solution AS-4 (Tokuyama Corporation, Japan) ionomer solution in 1-propanol using magnetic stirring and ultrasonication. To obtain a catalyst-coated substrate for the electrodes, the as-prepared ink was coated onto the surface of carbon paper using a hand-spray method with the aid of a spray gun. The Pt loading and ionomer content in the catalyst layer were ~0.50 mg/cm² and ~20 wt.%, respectively. The electrode size was 2.25 cm × 2.25 cm (~5 cm²).

Fuel cell testing was conducted with a commercial fuel cell testing system. The 5 cm² MEAs were mounted in a 2.25 × 2.25 cm test fixture containing two graphite blocks with machined single serpentine flow channels and two gold-coated current collector plates. The fuel cell performance was measured at a cell temperature of 50 °C. The anode/cathode humidifier temperatures were controlled to be a little bit higher than cell temperature in order to achieve full humidification (RH=100%). The fully humidified pure hydrogen and oxygen were supplied into the anode with a required flow rate of 200 SCCM **without back pressure**. The MEA was "activated" by operating at high current density (potentiostatic cell discharge at 100 mV) until current density increased to a maximum and constant level (normally 30 min to 1 hour). After full activation, fuel cell polarization curve was measured under galvanostatic mode, i.e. holding the fuel cell at serial constant currents for 3 min. The cell voltage as a function of current density was recorded using fuel cell testing software.

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Keywords: click chemistry • 1,2,3-triazole • anion exchange membranes • alkaline fuel cells • anion transport

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Anion transport facilitator: Clicked 1,2,3-triazoles incorporated into anion exchange membranes (AEMs) provide more sites to form efficient continuous hydrogen-bond networks for anion transport. Such molecular structures show a dramatic enhancement in anion conductivity compared with typical AEMs without triazole groups.

Nanwen Li,* Michael, D. Guiver,
Wolfgang H Binder*

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**Toward High Conductivity in Anion
Exchange Membranes for Alkaline
Fuel Cell Application**