Beneficial use of rotatable-spacer side-chains in alkaline anion exchange membranes for fuel cells

Yuan Zhu^a, Liang Ding^a, Xian Liang^a, Muhammad A. Shehzad^a, Lianqin Wang^b, Xiaolin Ge^a, Yubin He^a, Liang Wu^{a,*}, John R. Varcoe^b and Tongwen Xu^{a,*}

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Side-chain-type polymer architectures have been extensively studied for development of highly conductive fuel cell membranes. However, the commonly used rigid, hydrophobic spacers (between the ionic end-group and polymer backbone) limit self-assembly of ionic side-chains and, therefore, ion transport. Herein, we report a flexible, hydrophilic side-chain-type anion exchange membrane (AEM), where ethylene oxide spacers are incorporated into imidazolium-containing cationic side-chain. AFM and SAXS analysis confirm that the flexible spacers facilitate self-assembly of the ionic side-chain to form continuous conducting channels. Most importantly, both *in situ* FTIR spectroscopy and molecular dynamic theory simulations indicate that the ethylene oxide spacers are capable of hydrogen bonding to both H₂O molecules and hydrated OH⁻ ions. This unique auxiliary function facilitates both ion and H₂O transport during fuel cell operation. The resultant AEM exhibits a peak power density of 437 mW cm⁻² at 65 °C when tested in a H₂/O₂ single-cell anion-exchange membrane fuel cell, which is among the highest reported for comparable side-chain-type AEMs.

Introduction

With the sustainability and environmental issues centered around the use of fossil fuels, the world desperately needs highly efficient and clean energy conversion and storage devices, e.g. lithium-ion battery,^{1,2} sodium-ion battery,^{3,4} potassium-ion battery,⁵ fuel cell and flow battery. Among them, fuel cell technology,⁶ with the advantages of high energy efficiency and minimal harmful local emissions, has attracted a lot of attention over the past decades.^{7,8}

However, deployment of proton-exchange membrane fuel cells (PEMFC) is still being hampered by the high cost of commercial proton-exchange membrane (PEM) and the dependence on precious, scarce Pt-based catalysts.⁹ Conversely, anion-exchange membrane fuel cells (AEMFC), which can potentially use non-precious metal catalysts, e.g. Ni-, Co-, Fe-, and Mn-based catalysts, are promising alternatives to PEMFCs (especially in the portable/stationary/back-up power sectors).¹⁰⁻¹²

^a CAS Key Laboratory of Soft Matter Chemistry, Collaborative Innovation Centre of Chemistry for Energy Materials, School of Chemistry and Material Science, University of Science and Technology of China, Hefei 230026, P.R. China.
Email: liangwu8@ustc.edu.cn; twxu@ustc.edu.cn

^b Department of Chemistry, The University of Surrey, Guildford, Surrey GU2 7XH, United Kingdom.

†Electronic Supplementary Information (ESI) available: See DOI: 10.1039/x0xx00000x

As an essential component of AEMFCs, the anion-exchange membrane (AEM) serves to separate the fuel/oxidant gas supplies, conduct hydroxide ions (OH^-) from cathode to anode, and to diffuse water molecules from the anode (where they are generated) to the cathode (where they are faradaically consumed). The AEM's capacity to simultaneously transport both ions and H_2O molecules (in opposite directions) is a principle factor that impacts fuel cell (power) performance.^{13–17} However, the polymer framework can retard such transport processes, such that the effective mobility of the OH^- anions are much lower than that found in aqueous solutions. To overcome this common drawback, many efforts have been devoted to preparing AEMs that contain highly ordered “water channels”, where the water molecules in the center of these channels are bulk-like.^{18–20} Side-chain-type polymer architectures are a promising target model for forming such “water channels” in ion-exchange membranes. Ionic side-chains, commonly connected onto the polymer backbone *via* hydrocarbon “spacers”, are capable of self-assembling into ionic clusters. When hydrated, individual clusters can swell and connect with each other, leading to formation of continuous water channels.²¹ The flexibility and chemical composition of the ionic side-chains are known to directly affect AEM hydration, geometry and OH^- conductivity. Previous studies on side-chain-type AEMs containing rigid aryl spacers demonstrated improvements in OH^- conductivities over main-chain-type membrane (the latter is where ionic groups are connected onto the polymer backbones *via* short spacers, often C1 methylene ($-\text{CH}_2-$) groups).^{22–25} However, such spacers are hydrophobic and rigid, leading to limited OH^- conduction. Rigid spacer, such as hetero-atom-free alkyl linkage, often cause the side-chains to adopt an unfolded configuration, thereby dynamically hindering the self-assembly of ionic side-chains into clusters and limiting counter-ion mobility. Meanwhile, hydrophobic alkyl spacers are poor in mediating H_2O , and associated OH^- transport. One strategy to enhance hydrated OH^- transport is to increase the ionic content of the side-chains (2 – 4 cationic groups per side-chain) but this often causes undesirable, excessive dimensional changes between the hydrated and dehydrated states. In addition, densely co-located

Fig. 1 Synthesis of OBImPPO (flexible) and BImPPO (rigid) AEMs. The schematic illustrations (right) highlight the hypothesized effect of the side-chain molecular configuration on mobility.

cationic groups are also vulnerable to OH^- attack, which leads to the reduced AEM alkaline tolerance (degradation/fragmentation of the side-chains). Hence, the choice of ionic side-chains, particularly the

chemical composition of the spacer used, is a strategic target for AEM manufacturing, which is critical for achieving efficient AEMFC performance.

Hydrophilic and rotatable ethylene oxide groups provide the motivation for how we can increase the contribution of the side-chain flexibility to AEM morphology and enhanced anion conduction. It is widely recognized that ether groups can sternly interact with H_2O molecules^{26,27}. As Wu *et al.*²⁸ and Osanai *et al.*²⁹ have previously proposed, ether groups can hydrogen bond to H_2O , which improves the polymeric surfactant water absorbing ability. Moreover, ether-containing polymer electrolytes tend to exhibit higher chain motions owing to more facile rotation of the $\text{C}-\text{O}-\text{C}$ ether bonds; this molecular flexibility reduces the glass transition temperature (T_g) of a polymer, which can promote the transport of ions (e.g. in Li^+ conducting polyelectrolytes).³⁰ For AEM manufacturing, incorporation of flexible side chain also exhibits unique benefits on membrane performance.^{31–34}

Inspired by these prior observations, we present the concept of incorporating hydrophilic and rotatable ethylene oxide spacer into the ionic side-chains to improve an AEM's ion conductivity. A typical synthesis of the polyelectrolyte containing rotatable ethylene oxide side-chains (OBImPPO) is illustrated in Fig. 1. Excess 1, 2-dimethylimidazole was reacted with 1, 2-bis(2-chloroethoxy)ethane to yield 1,2-bis(2-(2-methylimidazole)ethoxy)ethane where the ethylene oxide spacer separates the two imidazole groups. One of these imidazole groups was then functionalized with methyl iodide, while the remaining (non-ionic) imidazole group was used attach the side chain onto the polymer backbone using a one-step Menshutkin reaction. Additionally, a benchmark BImPPO AEM containing rigid alkyl spacers was prepared for comparison. The effect of inclusion of rotatable ethylene spacers into the AEM, on properties such as ionic conductivity, membrane morphology, and H_2/O_2 AEMFC performance, is presented and discussed.

Experimental

Materials.

Poly(2,6-dimethyl-1,4-phenyleneoxide) (PPO), *N*-bromosuccinimide (NBS), azobisisobutyronitrile (AIBN), chlorobenzene, ethanol, 2-methylimidazole, potassium hydroxide (KOH), acetonitrile, 1,6-dibromohexane, dichloromethane, anhydrous sodium sulfate (NaSO_4), dimethylsulfoxide (DMSO), methyl iodide, tetrahydrofuran (THF), acetone, *N*-methylpyrrolidone (NMP) were all used as purchased.

Bromomethylation of PPO (BPPO).

PPO (2.0 g, 17 mmol) was dissolved in chlorobenzene (50 ml) in a two-necked flask. Under Ar atmosphere, NBS (1.2 g, 6.7 mmol) and AIBN (0.10 g, 0.61 mmol) were added into the solution and the mixture was heated at 130 °C with stirring for 4 h. The solution was then cooled to room temperature and poured into excess ethanol (500 ml) to form a fibrous precipitate. After washing with ethanol (5 × 50 ml), the obtained precipitate was dried in a vacuum oven for another 24 h. The ^1H NMR spectrum of the resulting bromomethylated poly(2,6-dimethyl-1,4-phenyleneoxide) (BPPO) is shown in Fig. S1.

Synthesis of 1,6-bis(2-methylimidazole)hexane (Blm).

2-methylimidazole (1.6 g, 20 mmol) and KOH (2.2 g, 40 mmol) were dissolved in acetonitrile (20 ml) and the mixture was stirred for 30 min. 1,6-dibromohexane (2.4 g, 10 mmol) was then added dropwise to the solution and the resulting mixture was stirred at 55 °C for 24 h. After removal of solvent by evaporation, 60 ml dichloromethane was added to the residue to extract the product and the unwanted precipitate was removed by centrifugation. The organic layer was washed with deionized water (5 × 50 ml) and dried with anhydrous NaSO₄. A viscous yellow liquid was obtained by evaporating the solvents. The ¹H NMR spectrum of Blm is shown in Fig. S2.

Synthesis of 1, 2-bis(2-(2-methylimidazole)ethoxy)ethane (OBlm).

2-methylimidazole (1.6 g, 20 mmol) and KOH (2.2 g, 40 mmol) were dissolved in DMSO (20 ml) and the mixture was stirred for 30 min. 1,2-bis(2-chloroethoxy)ethane (1.9 g, 10 mmol) was then added dropwise to the solution and the mixture was stirred at 75 °C for another 24 h. After cooling to room temperature, the mixture was poured into 150 ml deionized water and extracted with dichloromethane (5 × 30 ml). The organic layer was collected, washed with deionized water (5 × 30 ml) and dried with anhydrous NaSO₄. After evaporation of solvent, OBlm was obtained as a pale viscous oil. The ¹H NMR spectrum is shown in Fig. S3.

Synthesis of 1,2-dimethyl-3-(6-(2-methylimidazole)hexyl)-imidazolium (Blm-Me).

1.3 g Blm (4.7 mmol) was dissolved in 40 ml THF at room temperature. 0.29 ml methyl iodide (4.7 mmol), diluted with 10 ml THF, was then added dropwise into the Blm solution with stirring. After 12 h of continued stirring, the resulting precipitate was collected and washed with THF (3 × 40 ml). Then, 50 ml acetone was added to dissolve the monomethylated product. The organic layer was collected and the solvent was then removed. Blm-Me was obtained as a pale solid. The synthetic procedure of OBlm-Me was similar with that of Blm-Me (same ratio of MeI to reactant). The ¹H NMR spectra of Blm-Me and OBlm-Me are shown in Fig. S4 and Fig. S5.

Synthesis of BlmPPO and OBlmPPO.

0.30 g BPPO (D_{Br} = 25 %) was dissolved in 6.0 ml NMP at room temperature. Under stirring, 0.50 g Blm-Me was added to the solution and the mixture was heated at 50 °C for 12 h. The solution was then cast onto a clean glass pane to evaporate the solvent and the obtained AEM was immersed into deionized water to remove residual Blm-Me. The synthetic procedure of OBlmPPO was similar with that of BlmPPO. The ¹H NMR spectra of BlmPPO and OBlmPPO are shown in Fig. S6 and Fig. S7.

Characterizations.

¹H NMR spectra were recorded using a Bruker 510 instrument (400 MHz for ¹H). CDCl₃, CD₃OD and DMSO-*d*₆ were employed as solvents whereas the internal reference was tetramethylsilane (TMS). The nano-phase separation geometry images of membranes were obtained by using a Veeco diinnova SPM tapping mode Atomic Force Microscope (AFM). Small-angle X-ray scattering (SAXS) data was recorded on an Anton Paar SAXess mc2 instrument. An Osmic microfocus Cu K_α source and a parallel beam optic were employed. *In situ* FTIR spectra was recorded using a NICOLET iS10 of Thermo

Fisher Scientific. A moistened sample of AEM, where the surface water was completely removed using cotton, was fixed between two CaF₂ optical plates. The device was heated from 20 °C to 65 °C over 5 min and maintained at 65 °C for a further 55 min, during which the infrared absorbance of the AEM was recorded with an interval of 1 min per measurement.

Water uptake (WU) and swelling ratio (SR).

AEM samples in the Br⁻ form were saturated *via* immersion in deionized water for 24 h at room temperature. The residual water on surface was then wiped away with cotton wool and the length and weight of humid membrane were quickly recorded (*L_{wet}* and *W_{wet}*). Then, the same samples were placed in a vacuum oven at 60 °C for 48 h, after which the length and weight of dried membrane were recorded (*L_{dry}* and *W_{dry}*). The gravimetric water uptake and dimensional swelling ratio were calculated using:

$$\text{Water uptake (wt\%)} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\%$$

$$\text{Swelling ratio (L\%)} = \frac{L_{\text{wet}} - L_{\text{dry}}}{L_{\text{dry}}} \times 100\%$$

Ion exchange capacity (IEC).

The ion exchange capacity of each AEM was calculated using Mohr's titration method and confirmed using elemental analysis.

For the titration experiments, a sample of completely dried AEM sample (weight was recorded as *W_{dry}*) was immersed in aqueous NaCl (1.0 M) solution for 24 h at room temperature. After this ion exchange procedure, the AEM sample was frequently washed with deionized water for a further 24 h (to remove all traces of residual Cl⁻ anions). The AEM sample (in Cl⁻ form) when then was immersed in aqueous Na₂SO₄ (0.50 M) solution for 12 h to displace the Cl⁻ anions with SO₄²⁻. Finally, the collected solution was titrated using aqueous AgNO₃ (0.010 M) solution using K₂CrO₄ as a colored indicator. The volume of AgNO₃ solution consumed was recorded as *V_{Ag}* and the IEC value was calculated using:

$$\text{IEC} = \frac{V_{\text{Ag}} \times 0.01}{W_{\text{dry}}}$$

For elemental analysis, a completely dry membrane samples were heated in a Flash EA 1112 elemental analyser to calculate the content of nitrogen (recorded as N %). The IEC value was calculated using:

$$\text{IEC} = \frac{N \% \times 1000}{28}$$

Hydroxide conductivity.

Membrane samples (1 × 4 cm) were immersed in aqueous NaOH (1.0 M) solution for 12 h at room temperature. After complete ion-exchange, the samples were thoroughly washed to remove residual OH⁻ ions and kept in the sealed sample bottles. The DI water in the bottle was degasified *via* N₂ bubbling for 20 min before being sealed to keep any CO₂ away from each OH⁻ form AEM sample. The OH⁻ ion conductivity of each AEM sample was measured by impedance spectroscopy with the standard four-point probe technique using an Autolab PGSTAT 30 (Eco Chemie, Netherland) and a Teflon conductivity cell. Each AEM sample was placed in the Teflon cell, which was equipped with two current collecting electrodes and two potential sensing electrodes. The testing

assembly was then placed inside an oven with controlled temperature and humidity. The conductivity measurement was conducted immediately to minimize errors due to the effect of CO₂ interferences. The testing was operated under galvanostatic mode with the frequency ranged 1 MHz to 100 Hz. The OH⁻ conductivity was calculated using:

$$\sigma = \frac{L}{R \times W \times T}$$

where L is distance between potential sensing electrodes (= 1 cm for the test cell used), R is the absolute ohmic resistance of the membrane, and W and T are width and thickness of the membrane, respectively.

Alkaline stability

AEM samples (1 cm × 4 cm) were immersed in aqueous NaOH (1 M) solution at 60 °C for increasing periods of time. Before conductivity testing, the samples were washed with deionized water for 24 h to remove residual OH⁻ ions. The hydroxide conductivity, IEC, water uptake and swelling ratios (as a function of increasing alkaline treatment time) were recorded to evaluate the alkaline stabilities.

Thermal stability

Thermogravimetric analysis (TGA) of the samples was conducted by

The previously synthesized quaternary ammonium functionalized poly(2,6-dimethyl-1,4-phenylene oxide)³⁵ ionomer solution (IEC = 2.0 mmol g⁻¹, 15 mg ionomer dissolved in 135 mg methanol) was dispersed in 700 mg. This ionomer solution was mixed with catalyst suspensions, which contained 28 mg commercial Pt/C (60 wt% in metal content), or 28 mg PtRu/C catalysts (60 wt% in metal content) and 150 mg deionized water for the cathode and anode inks, respectively. These catalyst inks were stirred vigorously for 24 h and then sprayed onto a Toray TGP-H-60 carbon paper to fabricate gas diffusion electrodes (GDEs). Each electrode area was 12.25 cm² and metal loadings in both anode and cathode was controlled to be 0.5 mg_{metal} cm⁻². The AEMs under test (thickness of 60 ± 10 μm) and the GDEs were immersed in aqueous NaOH (1.0 M) solution for 12 h at room temperature (to achieve ion exchange) followed by thorough washing with deionized water. Each AEM was sandwiched between an anode and cathode GDEs to fabricate membrane electrode assemblies (MEA). Single cell performance evaluation was achieved by using an 850E Multi Range fuel cell test station (Scribner associates, USA) in galvanic mode at multiple temperature. The flow rate of H₂ and O₂ (100 % RH) was controlled at 1000 ml min⁻¹ without backpressure on either electrode. The polarization and power density curves were recorded after the cell temperature had stabilized at 65 °C for 20 min. The MEA was activated by discharging at a constant voltage of 0.6 V at 65 °C. After the stabilization of

heating them from 30 °C – 600 °C under N₂ atmosphere at a heating rate of 10 °C min⁻¹.

Mechanical properties

AEM samples were immersed in deionized water or heated at 80 °C for 24 h to obtain fully humidified or dry samples, respectively. The tensile strength, elongation at break and Young's modulus were measured using dynamic thermomechanical analysis (DMA Q800).

H₂/O₂ Single-cell performance.

current density, the power density over operating time was recorded with an interval of 10 seconds.

Simulation studies.

The Probability density distribution of the polymer side-chain was carried out by using LAMMPS-based molecular dynamic theory. The cubic simulation boxes, which included 32 chains of polymer with 10 monomers, were build using the Amorphous Cell module and geometrically optimized using the Forcite module in Material

(a)

(b)

Studios software (the chains and simulation boxes was shown in Figure S8). The systems were relaxed for 500 ps with a time step size of 0.5 fs for the constant NTP ensembles at 300 K and 1 atm under PCFF force field in LAMMPS. Ultimately, the coordinate of the side-chain was recorded and was transformed into a probability density distribution. The binding energy between side-chain and hydrated hydroxide ions was calculated by using of Blends module in Material Studios. All the molecular models were built under configuration optimization (shown in Figure S9). The molecular dynamic process was operated under PCFF force field with an energy bin width of 0.2 kcal mol⁻¹ at 298K.

Results and discussion

Benefits of rotatable ethylene oxide spacer for membrane nano-scale geometry

The hydrophobic/hydrophilic nano-phase separation geometry of the AEMs were investigated using AFM phase analysis. Fig. 2(a,b) show phase images of BImPPO, OBImPPO, where bright regions correspond to the hydrophobic polymer backbones aggregation and the dark regions hydrophilic side-chains assembly. For BImPPO, containing the rigid side-chains, the hydrophobic and hydrophilic domains show a large variance in their sizes (with channels blocking off each other), indicating poor self-assembly and unoptimized formation of ion conductive channels. In contrast, the OBImPPO, with flexible ethylene oxide spacers, exhibits a well-defined morphology with hydrophobic/hydrophilic nano-phase-separation. Fig. 4 a) The time-dependent *in situ* FTIR spectroscopy of hydrated OBImPPO (IEC = 2.1 mmol g⁻¹, immobilized between two CaF₂ optical plates) recorded during heating to 65 °C (heating rate = 9 °C min⁻¹). b) The binding energy (at 298 K) between side-chains and the hydrated OH⁻ ions (with various hydrated numbers) as calculated using molecular dynamic theory simulations where a negative binding energy indicates a spontaneous affinity between cationic-containing side-chains and hydrated OH⁻ ions: blue atoms = nitrogen, red and yellow = oxygen, white = hydrogen, gray = carbon, and the red dotted line = H-bond interactions.

The inter-connected hydrophilic domains facilitate the formation of continuous ion channels of relatively constant size, which enables efficient ion transport.³⁶ To more quantitatively investigate the size

adjust margins

ARTICLE

of ion channels, OBImPPO was analyzed using small angle X-ray scattering (SAXS). As shown in Fig. 2(c), a broad, distinct scattering intensity peak was observed at *ca.* 1.5 nm⁻¹ with the corresponding length scale of periodic structure is 4.2 nm ($d = 2\pi/q$, where, q was abscissa corresponding to the intensity peak), which is consistent with the mean size of hydrophilic domains observed in the AFM image.

The dissimilar abilities of the side-chains to self-assemble (BImPPO vs. OBImPPO) is responsible for the different morphologies. Generally, nano-phase segregation results from the incompatibility between the hydrophobic polymer backbone and hydrophilic (ionic) side-chain. Although the thermodynamic driving force for this process is similar, the kinetics are significantly different. The flexibility of side-chain, commonly affecting the freedom of movement during self-assembly, plays an essential role in the formation of ionic channels. The spatial distribution of the side-chains were recorded using molecular dynamic simulations with transformation of the 3D statistic into a 2D representation using d and θ to evaluate the extension and bending of the side-chains (see Fig. 3(a)). Fig. 3(b) and (c) show the joint probability density distribution contour maps for the OBImPPO and BImPPO side-chains, respectively. The BImPPO side-chains, with a deeper red zone in Fig. 3(c), exhibits a much more concentrated spatial probability density distribution compared to OBImPPO. This demonstrates that the more rigid alkyl side-chain is subjected to greater constraints where thermal molecular motions are suppressed, which invariably inhibits self-assembly (a disadvantage when it comes to formation of ion channels). Conversely, the higher flexibility of the OBImPPO side-chains, with a more diffuse probability distribution, leads to enhanced spatial mobilities and self-assembly of the ionic clusters, facilitating a more regular conformation of ion channels for improved conductivity (see Fig. 2(a)).

Rotatable ethylene oxide spacer facilitates hydroxide ions (OH⁻) transport

In addition to providing the benefit of enhanced flexibility (for forming ion channels), the ethylene oxide spacers can provide a desirable contribution towards facilitated ion transport. It is widely recognized that hydrophobic alkyl spacers have weak bonding affinities with water molecules and ions such as hydroniums, thereby contributing little in ion transport.²² Incorporation of hydrophilic units (*e.g.* alkyl ether groups in this study) permits formation of hydrogen bonds between the polymer side-chains and H₂O molecules and hydrated OH⁻ ions, which is expected to enhance ion conduction. To confirm this assumption, *in-situ* FTIR spectroscopy, recorded during heating to 65 °C, was employed to study the affinity of H₂O molecules and the ethylene oxide side-chain groups of the OBImPPO AEM (IEC = 2.1 mmol g⁻¹, immobilized between two CaF₂ optical plates). As shown in Fig. 4(a), the absorbance of the C–O–C bands (1000 – 1200 cm⁻¹) exhibited a

sharp decline during the first 20 min of heating but then plateaued with retention of absorbance at $t > 40$ min. Since the infrared absorption of free water and the ether groups do not interfere with each other (the *in situ* FTIR spectroscopy of free water is shown in Fig. S10), these observations are characteristic of ether group dehydration.

Hence, the hydrophilic ether groups in polymer side chain have an intrinsic affinity with H_2O molecules, which is consistent with water uptake and dimensional swelling data (see later in Fig. 5(a) and (b)) Fig. 5 a) Water uptakes and b) dimensional swelling ratios of the BlmPPO and OBlmPPO AEMs at elevated temperature. c) OH^- conductivities of the OBlmPPO and BlmPPO AEMs. d) OH^- conductivities of OBlmPPO ($\text{IEC} = 2.1 \text{ mmol g}^{-1}$) and BlmPPO ($\text{IEC} = 2.1 \text{ mmol g}^{-1}$) as a function of temperature.

The OBlmPPO AEMs have slightly higher water uptake and swelling ratio compared to BlmPPO of equal IECs. The hydrophilic ethylene oxide spacers are expected to be highly associated with the hydrated OH^- ions in the self-assembled ionic channels. Fig. 4(b) shows the binding energies of the interactions between side-chain molecule and hydrated OH^- anions, calculated using molecular dynamics theory simulation. The binding energy of OBlmPPO is more negative than that of BlmPPO, especially when OH^- hydration numbers increase: the increasing discrepancy between the two types of side-chains indicates the increasingly favorable interactions between the hydrated OH^- anions and the OBlmPPO side-chains. As ether groups are prone to absorb H_2O , they serve as active sites during transport of hydrated OH^- ions, which extends the ion conduction region from the positively charged imidazolium groups to the whole side-chain, thereby enhancing ion conduction. As shown in Fig. 5(c) and (d), the OH^- conductivity of OBlmPPO ($\text{IEC} = 2.1 \text{ mmol g}^{-1}$) reaches 45 mS cm^{-1} at room temperature. BlmPPO ($\text{IEC} = 2.1 \text{ mmol g}^{-1}$) exhibits lower conductivities than OBlmPPO ($\text{IEC} = 2.1 \text{ mmol g}^{-1}$) at all temperatures in the range $25 - 60^\circ\text{C}$.

Benefits of rotatable ethylene oxide spacer for fuel cell performance

Considering the benefits of using ethylene oxide spacers (discussed above), OBlmPPO type AEMs are expected to achieve improved fuel cell performances, hence, H_2/O_2 single cell AEMFC tests with the exactly same electrodes (same catalysts, ionomer and fabrication process) were conducted at 65°C . As shown in Fig. 6(a), the open circuit voltages recorded with OBlmPPO ($\text{IEC} = 2.1 \text{ mmol g}^{-1}$) and BlmPPO ($\text{IEC} = 2.1 \text{ mmol g}^{-1}$) are close to the theoretical values (of 1.23 V), indicating that the AEMs do not suffer from significant fuel crossover.³⁷ The maximum power density with the BlmPPO AEM was 204 mW cm^{-2} , which is close to values of recently reported for side-chain-type AEMs (Fig. 6(b) and Table S2). Comparatively, the OBlmPPO AEM exhibits a significantly higher peak power density of

437 mW cm^{-2} , which is $2 \times$ the value recorded for the BlmPPO and amongst the highest values recently reported for side-chain-type AEMs (Fig. 6(b) and Table S2).^{13,23,35,38-44} Moreover, at a constant discharge voltage of 0.6 V , the power density of BlmPPO-2.1 drops from 202 mW cm^{-2} to 74 mW cm^{-2} (37 % of the initial value) in 3.4 h (Fig. 6c). In comparison, OBlmPPO-2.1 maintains 70 % of the initial IEC after 5 h (decreases from 352 mW cm^{-2} to 246 mW cm^{-2}). This decrease in power density results from the poor alkaline tolerance of the imidazolium cationic groups (details in Fig. S12). The degradation of imidazolium groups under alkaline conditions will decrease the ion transport efficiency of AEMs. OBlmPPO, with rotatable spacers, exhibits a much slower decline in both peak power density (discussed above) and in IEC values after aqueous alkaline treatment (Fig. 6(d)). This improvement in alkaline resistance is attributed to the presence of ethylene oxide spacers. Since ether groups improve the hydrophilicity of ionic side chain, generated OH^- ions are more hydrated (less nucleophilic) and can more easily diffuse into larger hydrophilic ion-conducting regions (where the local alkali concentration is diluted): both of these mitigate against the rapid degradation of cationic groups.⁴⁵ These results provide further evidence of the benefit to utilizing rotatable ethylene oxide spacers in side-chain-type AEMs. The OH^- ions that are continuously generated in the oxygen reduction reaction at the cathode side, can more easily conduct to the anode side *via* the above-mentioned interactions with both the hydrophilic cationic groups and ether spacer groups. This elongation of hydrophilicity around the whole of the side-chains leads to improved ion flux (cathode to anode) and H_2O back-diffusion (anode to cathode), thereby reducing both Ohmic and mass transport losses in the AEMFCs.

Conclusions

In summary, we propose a strategy of incorporating rotatable ethylene oxide spacers into the ionic side-chains of PPO-based imidazolium AEMs to improve OH^- anion conductivity. It was hypothesized that the improved flexibility increases the chain motions of the ether-containing side-chain to enhance the self-assembly process (formation of hydrated ion channels). The AFM and SAXS confirms a uniform nano-phase segregated morphology with continuous ion conductive channels. Most importantly, *in-situ* FTIR technique, combined with molecular dynamic theory calculations, proves that the presence of ethylene oxide spacer enhances the beneficial interactions between the hydrophilic side-chain and the hydrated OH^- anions. This unique character extends the ion conducting region to encompass the entire side-chains, which accelerates the efficiency of both ion and H_2O transport. This resulted in a notably high H_2/O_2 anion-exchange membrane fuel cell performance with 437 mW cm^{-2} peak power density.

Associated content

Electronic Supplementary Information (ESI)

^1H NMR spectra of synthesized compounds, molecular models in molecular dynamic theory simulation and summary of H_2/O_2 single fuel cell performances of recently reported AEMs.

Conflicts of interest

There are no conflicts to declare.

Fig. 6 (a) Polarization and power density curves of OBlmPPO ($\text{IEC} = 2.1 \text{ mmol g}^{-1}$) and BlmPPO ($\text{IEC} = 2.1 \text{ mmol g}^{-1}$) in H_2/O_2 single cell AEMFC tests at 65°C (PtRu/C anodes and Pt/C cathodes, both with metal loadings = 0.5 mg cm^{-2} , H_2 and O_2 flow rates of 1 L min^{-1} and $\text{RH} = 100\%$). (b) The AEMFC peak power densities at 60°C as a function of room temperature OH^- conductivities for recently reported AEMs. (c) Power densities of OBlmPPO-2.1 and BlmPPO-2.1 in H_2/O_2 single fuel cell held at 0.6 V as a function of operating time at 65°C . (d) IEC values of OBlmPPO-2.1 and BlmPPO-2.1 as a function of alkaline treatment time (aged in aqueous NaOH (1 M) at

Acknowledgements

This research was supported by the National Natural Science Foundation of China (Nos. 21720102003, 21522607, 51934203) and the Fundamental Research Funds for the Central Universities. Lianqin Wang's and John Varcoe's time was funded by EPSRC grant EP/M014371/1.

Notes and references

- H. G. Wang, S. Yuan, D. L. Ma, X. B. Zhang and J. M. Yan, *Energy Environ. Sci.*, 2015, **8**, 1660-1681.
- T. Sun, Z. J. Li, H. G. Wang, D. Bao, F. L. Meng and X. B. Zhang, *Angew. Chem.* 2016, **128**, 10820 – 10824.
- H. G. Wang, W. Li, D. P. Liu, X. L. Feng, J. Wang, X. Y. Yang, X. B. Zhang, Y. Zhu and Y. Zhang, *Adv. Mater.*, 2017, **29**, 1703012.
- H. Wang, S. Yuan, D. Ma, X. Huang, F. Meng and X. Zhang, *Adv. Energy Mater.*, 2014, **4**, 1301651.
- Y. H. Zhu, Y. B. Yin, X. Yang, T. Sun, S. Wang, Y. S. Jiang, J. M. Yan and X. B. Zhang, *Angew. Chem. Int. Ed. (Engl)*, 2017, **56**, 7881-7885.
- M. Z. Jacobson, W. G. Colella and D. M. Golden, *science*, 2005, **308**, 1901-1905.
- Y. J. Wang, J. Qiao, R. Baker and J. Zhang, *Chem. Soc. Rev.* 2013, **42**, 5768-5787.
- U. Lucia, *Renew. Sust. Energ. Rev.* 2014, **30**, 164-169.
- R. Borup, J. Meyers, B. Pivovar, Y. S. Kim and R. Mukundan, *Chem. Rev.*, 2007, **107**, 3904-3951.
- S. D. Poynton, J. P. Kizewski, R. C. T. Slade and J. R. Varcoe, *Solid State Ionics*, 2010, **181**, 219-222.
- N. Wagner, M. Schulze and E. Gülzow, *J. Power Sources*, 2004, **127**, 264-272.
- P. A. J. R. Varcoe, D. R. Dekel, A. M. Herring, M. A. Hickner, P. A. Kohl, A. R. Kucernak, W. E. Mustain, K. Nijmeijer, K. Scott, T. Xu and L. Zhuang, *Energy Environ. Sci.* 2014, **7**, 3135-3191.
- L. Zhu, J. Pan, Y. Wang, J. Han, L. Zhuang and M. A. Hickner, *Macromolecules*, 2016, **49**, 815-824.
- K. H. Lee, D. H. Cho, Y. M. Kim, S. J. Moon, J. G. Seong, D. W. Shin, J.-Y. Sohn, J. F. Kim and Y. M. Lee, *Energy Environ. Sci.* 2017, **10**, 275-285.
- J. S. Olsson, T. H. Pham and P. Jannasch, *Adv. Funct. Mater.* 2018, **28**, 1702758.
- T. Zhu, S. Xu, A. Rahman, E. Dogdibegovic, P. Yang, P. Pageni, M. P. Kabir, X. D. Zhou and C. Tang, *Angew. Chem. Int. Ed.* 2018, **57**, 2388-2392.
- J. Pan, C. Chen, Y. Li, L. Wang, L. Tan, G. Li, X. Tang, L. Xiao, J. Lu and L. Zhuang, *Energy Environ. Sci.*, 2014, **7**, 354-360.
- K. N. Grew and W. K. S. Chiu, *J. Electrochem. Soc.* 2010, **157**, B327-B337.
- C. Chen, Y.-L. S. Tse, G. E. Lindberg, C. Knight and G. A. Voth, *J. Am. Chem. Soc.* 2016, **138**, 991-1000.
- T. HiromitsuTakaba, TomoakiShimizu, Md.KhorshedAlam, *J. Membr. Sci.* 2017, **522**, 237-244.
- V. K. Chen Wang, Dongsheng Wu, Rylan Bledsoe, and S. J. P. a. G. Duscher, *J. Mater. Chem. A*, 2013, **1**, 938-944.
- C. X. Lin, Y. Z. Zhuo, A. N. Lai, Q. G. Zhang, A. M. Zhu and Q. L. Liu, *Rsc Adv.* 2016, **6**, 17269-17279.
- W.-H. Lee, Y. S. Kim and C. Bae, *ACS Macro Lett.* 2015, **4**, 814-818.
- A. H. N. Rao, S. Nam and T.-H. Kim, *J. Mater. Chem. A*, 2015, **3**, 8571-8580.
- X. Li, G. Nie, J. Tao, W. Wu, L. Wang and S. Liao, *ACS Appl. Mater. Inter.*, 2014, **6**, 7585-7595.
- R. París, J. M. Barrales-Rienda and I. Quijada-Garrido, *Polymer*, 2009, **50**, 2065-2074.
- M. Horstmann, M. Urbani and W. S. Veeman, *Macromol. Symp.* 2004, **205**, 129-142.
- H. Lai and P. Wu, *Polym. Chem.* 2013, **4**, 3323-3332.
- S. Osanai, G. Yamada, R. Hidano, K. Beppu and K. Namiwa, *J. Surfactants Deterg.* 2009, **13**, 41-49.
- H. Zhang, C. Li, M. Piszcz, E. Coya, T. Rojo, L. M. Rodriguez-Martinez, M. Armand and Z. Zhou, *Chem. Soc. Rev.* 2017, **46**, 797-815.
- X. Gong, X. Yan, T. Li, X. Wu, W. Chen, S. Huang, Y. Wu, D. Zhen and G. He, *J. Membr. Sci.* 2017, **523**, 216-224.
- Y. Chen, Y. Tao, J. Wang, S. Yang, S. Cheng, H. Wei and Y. Ding, *J. Polym. Sci. Part A: Polym. Chem.* 2017, **55**, 1313-1321.
- S. C. Price, X. Ren, A. M. Savage and F. L. Beyer, *Polym. Chem.* 2017, **8**, 5708-5717.
- E. N. Hu, C. X. Lin, F. H. Liu, X. Q. Wang, Q. G. Zhang, A. M. Zhu and Q. L. Liu, *J. Membr. Sci.* 2018, **550**, 254-265.
- Y. Zhu, Y. He, X. Ge, X. Liang, M. A. Shehzad, M. Hu, Y. Liu, L. Wu and T. Xu, *J. Mater. Chem. A*, 2018, **6**, 527-534.
- D. W. Shin, S. Y. Lee, C. H. Lee, K.-S. Lee, C. H. Park, J. E. McGrath, M. Zhang, R. B. Moore, M. D. Lingwood, L. A. Madsen, Y. T. Kim, I. Hwang and Y. M. Lee, *Macromolecules*, 2013, **46**, 7797-7804.
- W. Li, J. Fang, M. Lv, C. Chen, X. Chi, Y. Yang and Y. Zhang, *J. Mater. Chem.* 2011, **21**, 11340-11346.
- C. X. Lin, X. Q. Wang, L. Li, F. H. Liu, Q. G. Zhang, A. M. Zhu and Q. L. Liu, *J. Power Sources*, 2017, **365**, 282-292.
- X. Q. Wang, C. X. Lin, Q. G. Zhang, A. M. Zhu and Q. L. Liu, *Int. J. Hydrogen Energy*, 2017, **42**, 19044-19055.
- C. Xiao Lin, X. Qin Wang, E. Ning Hu, Q. Yang, Q. Gen Zhang, A. Mei Zhu and Q. Lin Liu, *J. Membr. Sci.* 2017, **541**, 358-366.
- M. Iravaninia, S. Azizi and S. Rowshanzamir, *Int. J. Hydrogen Energy*, 2017, **42**, 17229-17241.
- C. X. L. Dong Guo, En Ning Hu, Lin Shi, Faizal Soyekwo, Qiu Gen Zhang, Ai Mei Zhu, Qing Lin Liu, *J. Membr. Sci.* 2017, **541**, 214-223.
- J. Han, L. Zhu, J. Pan, T. J. Zimudzi, Y. Wang, Y. Peng, M. A. Hickner and L. Zhuang, *Macromolecules*, 2017, **50**, 3323-3332.
- D. Guo, A. N. Lai, C. X. Lin, Q. G. Zhang, A. M. Zhu and Q. L. Liu, *ACS Appl. Mater. Inter.*, 2016, **8**, 25279-25288.
- D. R. Dekel, M. Amar, S. Willdorf, M. Kosa, S. Dhara and C. E. Diesendruck, *Chem. Mater.*, 2017, **29**, 4425-4431.

Energy & Environmental Science

ARTICLE