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VS

Conventional

Alkaline Stable Pendant Type AEM

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Strategy to Construct Alkali Stable Anion Exchange Membranes Bearing Ammonium Groups via Flexible Spacers

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A novel strategy is provided to construct alkaline stable poly(phenylene oxide) based anion exchange membranes to alleviate cation-induced degradation. Facile and safe Suzuki-Miyaura coupling reaction was employed in grafting phenylpropyl bromide for the followed quaternization and alkalization. Enhanced hydroxide conductivity and suppressed water swelling were obtained.

The increasing energy demand and the depletion of conventional energy resource have raised an urgent issue. Fuel cell technology serves one of the most promising candidates to supply alternative energy in a clean and efficient way[1]. Fuel cells can directly covert chemical energy into electric energy with high efficiency and low pollution. Among them, polymeric electrolyte fuel cells deserve great research interests and great evolvements have been made. Typically, there are two kinds of polymeric electrolyte fuel cells, the proton exchange membrane fuel cell (PEMFC) and the anion exchange membrane fuel cell (AEMFC). Although the PEMFC is the most extensively explored, the commercialization of PEMFC has been hindered by its high cost (due partly to Nafion®), in-plane swelling and total dependence on Pt catalysts[2]. In contrast, AEMFC operated under alkaline conditions offers numerous advantages[3]. Those include easy water management and the adoption of high energy density liquid[4](such as methanol, hydrazine). Since OH⁻ ions are transported in the opposite direction to fuels, fuel crossover is sharply decreased. Most importantly, faster oxygen reduction reaction kinetics will be obtained under alkaline conditions and the catalysts are not subjected to corrosion as opposed to strong acidic environment. Although high power density could be obtained in PEMFC with low Pt loading and

Nafion®, non-precious metal catalysts can be employed to greatly reduce the cost of AEMFC[5].

Anion exchange membranes (AEMs) are the most critical component in an AEMFC. To date, various types of AEMs have been developed. These AEMs are synthesized by incorporating cationic function groups, such as ammonium[6, 7], phosphonium[8], imidazolium[9], metal ions[10] etc. in either an aromatic polymer backbone or an aliphatic polymer backbone. Since the initial attempt of employing AEM in AEMfs, the attack of hydroxide ions on the cationic head groups remains a major challenge. Degradation pathways including S_{N2} substitution, ylide formation and Hofmann elimination have been observed. Recently, the cation triggered polymer backbone scission raises another important issue. The 2D-NMR spectroscopy revealed the backbone degradation of polysulfone based AEM in alkali media via quaternary carbon hydrolysis and ether hydrolysis, leading to rapid failure [11]. This phenomenon was investigated by the density functional theory(DFT) modeling[12]. Modelling results confirmed that aryl-ether cleavage barrier (85.8 kJ/mol) was lower than that of the S_{N2} substitution on benzyl carbon (90.8 kJ/mol) leading to the favourable aryl-ether cleavage.

Inspired by this fact, scientists are currently searching for strategies to alleviate the cation-induced backbone degradation. Miyatake et al. synthesized anion conductive aromatic copolymers containing oligophenylene moieties as a scaffold for quaternized ammonium groups. The devoid of aryl ether bond in the cationic segments lead to the increased alkaline stability[13]. Zhuang et al. designed an effective method to alleviate the cation-induced backbone degradation by incorporating pendant quaternary ammonium(pQAPPO)[14]. Although enhanced chemical stability was observed, the introduction of additional amine and hydroxyl groups in the side chains generally lead to the increase in water swelling. Jannasch et al. functionalized poly (phenylene oxide) with quaternary ammonium groups via flexible alkyl spacers (PPO-7Q). Significantly enhanced hydroxide ion conductivity and far superior alkaline stability in relation to corresponding polymers with quaternary ammonium (QA) groups placed in benzylic

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positions directly on the backbone(quaternized poly(phenylene oxide), denoted as QPPO) were observed[15]. It provided a straight forward synthetic strategy to separate the cation groups from polymer backbone. Yet, extreme reaction conditions (BuLi, -78 °C) were required when lithium chemistry was involved. Therefore, there lies an urgent demand for a milder and straightforward synthetic strategy to construct alkali stable anion exchange membranes bearing pendant cationic head groups without causing unnecessary water swelling. Herein, we reported the strategy to construct anion exchange membranes with quaternary ammonium groups connected to the polymer scaffold via flexible spacers, which is different from the "tail-protected" anion exchange membrane to whose backbone the ammonium groups are directly attached[2]. We employed here the mild and high converting Suzuki-Miyaura coupling reaction[16, 17] to fulfil this goal. Detailed synthetic route is presented in Fig.1.
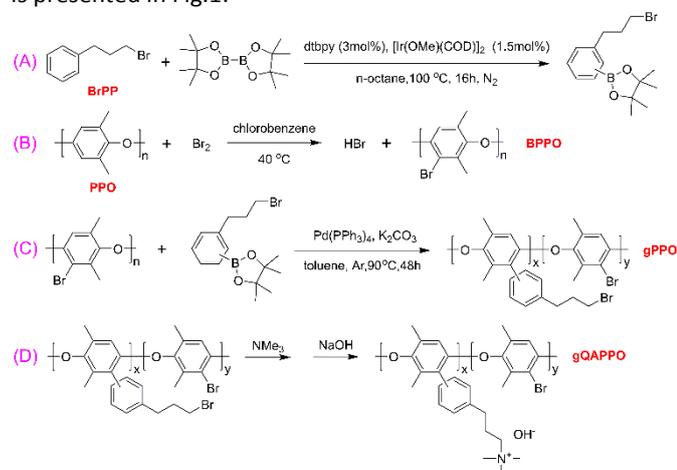

Fig. 1 Schematic for the (A) Iridium catalyzed Miyaura borylation of 1-bromo-3-phenylpropane (BrBP); (B) Bromination of poly (2, 6-dimethyl-1, 4-phenyleneoxide) (PPO); (C) Palladium catalyzed Suzuki coupling reaction between brominated PPO and borylated BrPP; (D) gPPO membrane quaternization and hydroxide exchange treatment

Firstly, borylated 1-bromo-3-phenylpropane (BBrPP) was synthesized via iridium catalysed Miyaura reaction (Fig. 1A). We choose this reaction because of its high conversion rate, safe and facile operation. The resulting products were confirmed by NMR spectroscopy. Since steric hindrance plays a determining role in the Miyaura borylation reaction, borylation will occur in the meta- and para- position as proved in Fig.2A.It is very convenient to adjust the borylated sites by adding steric hindrance and it is now undergoing (as depicted in Fig. S1). Nevertheless, at current stage, we believe the alkyl chain attached in para- or meta- position to polymer backbone would not make much influence. This assumption has already been confirmed[18]. Commercialized boronic acid can also be employed in this reaction as demonstrated in Fig. S2, which is now under investigating in this scope. Thus, extended AEM structure variety could be anticipated relating to the grafted small molecular compounds.

For the polymer counterpart, we began with the commercially available poly (2, 6-dimethyl-1, 4-phenyleneoxide) (PPO). PPO is one of the most important engineering plastics

and possesses excellent mechanical, thermal and chemical properties. In the earlier stage, chloromethylation procedure followed by substitution of the chloromethyl group with trimethylamine to form QA groups was essential in preparing AEMs when PPO was utilized as starting materials. However, the chloromethyl methyl ether used in chloromethylation procedure is carcinogenic and precise control of the degree and location of functionalization is usually difficult. The PPO based AEM was not prevailing until Xu et al. reported the bromomethylation of PPO by bromine at high temperature[19]. The bromomethylation at benzylic position is accompanied by the bromo-substitution reaction at the aryl position, which is redundant despite of its ability to balance hydrophobicity and hydrophilicity. In this contribution, Suzuki coupling reaction is conducted at aryl bromide sites. The commonly unreactive groups serve here as functionality which would lead to the fabrication of series of PPO based membranes. Bromination of PPO by bromine at moderate temperature yields the corresponding BPPO (Br_2 is volatile, Fig. 1B), which is also commercially reachable. It was conducted here to demonstrate the accessibility and to serve as an important example of PPO functionalization via aryl bromination. Compared with traditional bromomethylation reaction, aryl bromination offers advantage including milder reaction condition, easy handling, high conversion rate, precise functionalization location and easily tuned bromination degree.

The flexible alkyl bromide was attached to the BPPO main chains via a one-step Suzuki coupling reaction. The resulting gPPO was aminated, solution cast and ion exchanged to prepare the hydroxide conductive gQAPPO. All the polymers including PPO, BPPO, gPPO and gQAPPO were characterized by NMR spectroscopy and the spectra are presented in Fig.2. The shift from 6.5 ppm to 6.15 ppm of benzene ring and the splitting of methyl groups at 2.08 ppm indicates the success in aryl bromination. The disappearance of peak at 6.5 ppm implies that all the repeating units are brominated. No observation of peaks at 4.5 ppm suggests the absence of benzylic bromide. The successful grafting of BBrPP onto the BPPO backbone is evidenced by the new peaks at 3.4 ppm and 2.8 ppm in the NMR spectrum of gPPO. These hydrogens are derived from BBrPP. When gPPO was aminated, the new peak at 3.1 ppm which belongs to alkyltrimethyl ammonium head groups can be observed indicating the success of quaternization. By varying the amount of trimethylamine added in quaternization reaction, two gQAPPO membranes were made with different degree of amination. The ion exchange capacity values (IEC) were determined by conventional titration. The theoretical IEC value is 2.65 mmol/g if all the Br groups are transferred.

Sufficient hydroxide conductivity is the most critical in potentially adopting the as-prepared AEM in AEMFC. To examine its potentiality, the hydroxide conductivity of the gQAPPO membranes have been measured and presented in Fig.3. Over the entire temperature range, gQAPPO membranes exhibit satisfactory hydroxide conductivities and an increase in hydroxide conductivity is observed as temperature increases.
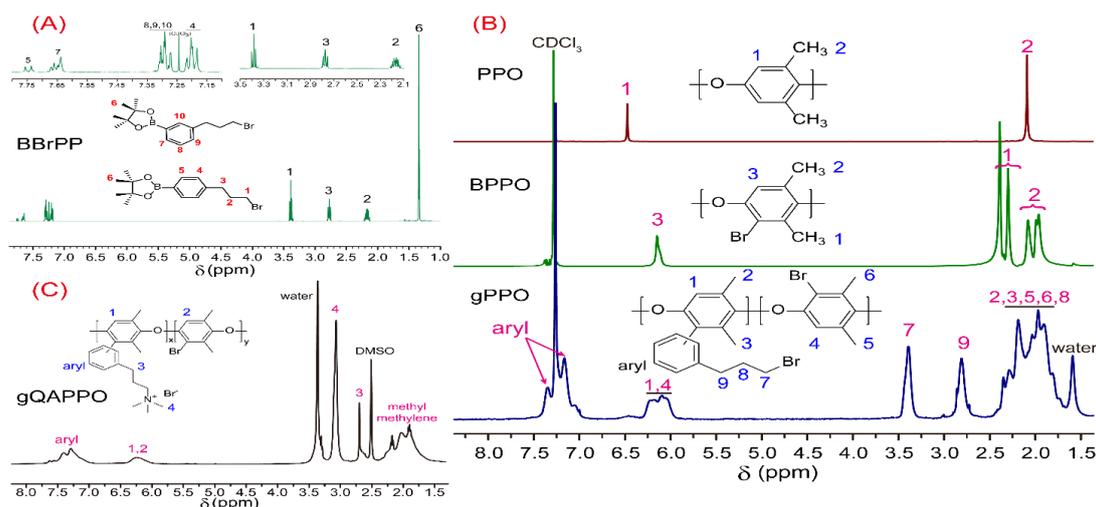
Fig. 2 NMR spectrum of (A)borylated 1-bromo-3-phenylpropane(BBrPP, in CDCl$_3$); (B)commercialized PPO, brominated PPO(BPPO) and flexible pendant chain grafted PPO(gPPO)(in CDCl$_3$); (C)gQAPPO anion exchange membrane (in Br$^-$ form, in DMSO). All chemical shifts are referenced to TMS.

The hydroxide conductivity of gQAPPO membrane (1.43 mmol/g) at 30 °C and 70 °C is 20.52 mS/cm and 38.26 mS/cm, respectively. In the meantime, increased hydroxide conductivity is obtained for membrane with higher IEC value. The as prepared gQAPPO membrane (1.78 mmol/g) exhibits a hydroxide conductivity of 27.02 mS/cm and 62.7 mS/cm at 30 °C and 70 °C, respectively. gQAPPO membrane developed here can be potentially applied in AEMFC. The hydroxide conductivities are compared with that from two separate sources of QPPO to which quaternary ammonium groups are directly attached. For QPPO membrane with IEC value of 1.5 mmol/g, the hydroxide conductivity is pretty low even at high temperature and can hardly meet the basic requirement of AEMFC [15]. In contrast, for the gQAPPO membrane with similar density of cationic groups, the hydroxide conductivity is several times higher. Apparently, the most straightforward method to increase hydroxide conductivity is by introducing more hydroxide conductive groups, i.e. increasing the IEC values of QPPO. Bai et al. reported QPPO membranes with IEC value of 1.97 mmol/g possessing hydroxide conductivity of 18.2 mS/cm at 60 °C [6]. For QPPO membrane with even higher cationic density (2.05 mmol/g), higher hydroxide conductivity is acquired [20]. Unfortunately, the highest conductivity acquired for QPPO at 80 °C is 40 mS/cm which can barely go beyond that of gQAPPO at 70 °C (1.43 mmol/g, 38.26 mS/cm). The aforementioned fact indicates that the cationic groups in gQAPPO membrane could transport OH$^-$ more effectively than that of QPPO. Additionally, the increase in IEC value of QPPO membrane will highly increase the polarity of the materials and even results in the dissolution in methanol [21]. It will limit the choices of fuel inside AEMFC and cause much sacrifice in dimensional stability of AEMs.

For a similar PPO scaffold functionalized with quaternary ammonium groups via flexible alkyl spacers, i.e. PPO-7Q (1.5 mmol/g), parallel hydroxide conductivities are observed at moderate temperatures. When the temperature is increased, gQAPPO membrane (1.78 mmol/g) exhibits higher hydroxide

conductivity. Compared with QPPO membranes, the higher OH$^-$ conductive nature of both PPO-7Q and gQAPPO can be attributed to the increased cation mobility, which leads to the enhanced micro-phase separation [15]. Noteworthily, compared with the development of PPO-7Q membrane, gQAPPO membrane reported here opened a new window in the strategy to construct long side-chain type AEM. It offers a facile procedure without employing extreme reaction conditions (such as -78 °C, BuLi). Most importantly, similar properties are obtained.
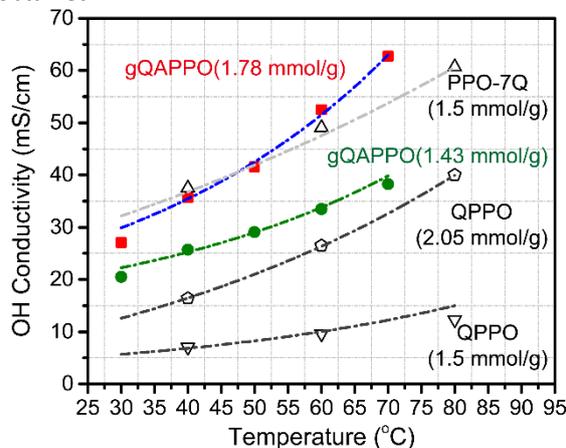

Fig. 3 Temperature dependence of hydroxide conductivity of gQAPPO membranes (1.78 mmol/g and 1.43 mmol/g), PPO-7Q membrane (1.5 mmol/g, conductivity data obtained from ref. 15) and QPPO membranes (1.5 mmol/g and 2.05 mmol/g, conductivity data obtained from ref. 15 and ref. 20, the chemical structure is shown in Fig. S5)

Water uptake is always a very important aspect of AEMs that one shall take into consideration. Excessive water uptake means increased membrane swelling and decreased membrane dimensional stability. It will do great harm to the fabrication of membrane electrode assembly and sometimes causes the mechanical failure. The water uptake of gQAPPO membrane (1.43 mmol/g) ranges from 31.26 wt%-49.91 wt% at 30 °C and 80 °C, respectively. For membranes with higher IEC value (1.78 mmol/g), higher water uptake is observed. Surprisingly, the

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highest water uptake does not exceed 55wt% indicating good dimensional stability. QPPO membrane with directly attached ammonium groups (1.97 mmol/g) exhibit a water uptake of 77wt%[6]. For pQAPPO membrane (2.23 mmol/g), the water uptake can reach up to 100 wt % at 80 °C[14]. Along with PPO-7Q membrane, gQAPPO membrane shows superior dimensional stability. In the meantime, lower water uptake implies a higher local cation concentration. That is to say water molecules are more effectively utilized or continuous hydroxide conductive pathways have been formed, which could be ascribed to the enhanced phase separation (Fig. S4). The incorporation of flexible spacers imparts the head groups with enhanced mobility which results in the formation of phase separated morphology. The dimensional stability of the membrane is also evidenced by the fact that the highest linear expansion ratio for gQAPPO membrane (1.43 mmol/g) is less than 17 % (Table S1). It should be noted that controlling IEC value via adjusting the usage of NMe_3 would leave unreacted alkyl bromide groups and it might have a profound influence on phase separation and membrane properties[22]. A better method to tune the membrane IEC value is to manipulate grafting degree in the Suzuki coupling reaction.
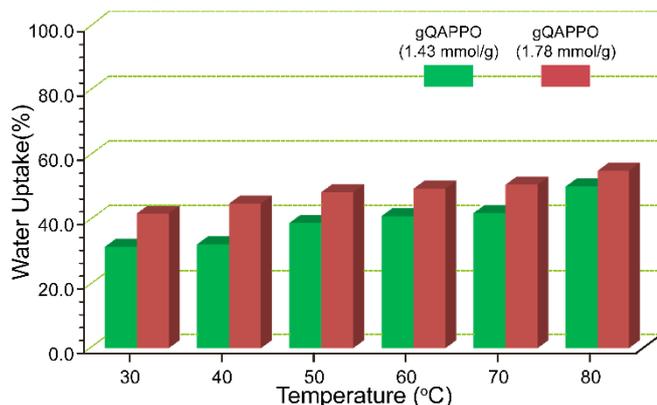

Fig. 4 Water uptake of gQAPPO membranes (1.43 mmol/g and 1.78 mmol/g) at varied temperatures

The gQAPPO membrane also exhibit great thermal stability (Fig. S3). Moreover, according to the report on PPO-7Q membrane, we believe that the incorporation of flexible spacer between the ammonium groups and the polymer backbone will result in the increase in chemical stability. The gQAPPO membrane (1.78 mmol/g) is immersed in 1M NaOH at 60 °C for 168h and the hydroxide conductivity remains around 90% of the original conductivity. However, we will present a thorough investigation on the chemical stability of gQAPPO membrane in accelerated degradation tests shortly. We intend to monitor the change in both membrane structure and the generation of degradation products via NMR spectroscopy. Currently, we are tuning the chain length between the ammonium groups and the polymer backbone to see what the impact will be on the hydroxide conductivity, water uptake and dimensional stability. The SAXS tests will also be referred to characterize the impact of spacer length on the micro-phase separation of the gQAPPO membrane.

In conclusion, we report here a facile, safer and straightforward synthetic strategy to construct alkali stable AEMs bearing ammonium groups via flexible spacers. Enhanced hydroxide conductivity and increased dimensional stability are observed for the resulting gQAPPO membrane. The method reported here will open up new possibilities for PPO functionalization via aryl bromination and offers novel synthetic strategy to construct alkali stable AEMs with various types of polymer backbone bearing cationic groups(such as phosphonium and imidazolium) via flexible spacers.

Acknowledgements

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