



An effective strategy to increase hydroxide-ion conductivity through microphase separation induced by hydrophobic-side chains



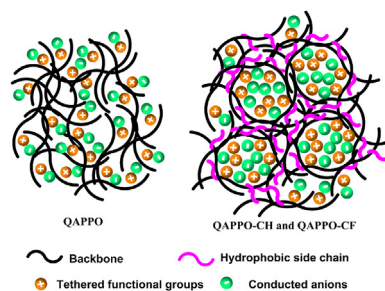
L. Zeng, T.S. Zhao*

Department of Mechanical and Aerospace Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong Special Administrative Region

HIGHLIGHTS

- An effective strategy to increase hydroxide-ion conductivity was introduced.
- The microstructure of ionomers was manipulated by grafting hydrophobic side chain.
- Well nano-phase separated domains with connected ionic channels were established.
- An ionic conductivity of 65 mS cm^{-1} was achieved in the self-aggregated ionomers.

GRAPHICAL ABSTRACT



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ABSTRACT

A highly conductive and durable anion exchange membrane (AEM) is an essential component for alkaline electrochemical conversion and storage systems. Contrary to the conventional wisdom that the ionic conductivity can be improved by increasing the ion exchange capacity (IEC) through a cross-linking process, in this work, a new approach to improve the ionic conductivity by enhancing the ionic mobility is adopted. The microstructure of quaternary ammonia poly (2, 6-dimethyl-1, 4-phenylene oxide) (QAPPO) is manipulated through grafting with hydrophobic side chains, which will drive the well-established hydrophilic/hydrophobic domains and nano-phase separated, well-connected ionic channels. As a result, the local hydroxide concentration is enhanced by the novel microstructure, thereby improving the ionic conductivity of the as-prepared ionomers. The as-prepared ionomers, denoted as self-aggregated QAPPO-CF, with an intermediate IEC value achieved an ionic conductivity of 65 mS cm^{-1} at 80°C , outperforming the QAPPO with an even higher IEC value. This result suggests that the microphase separation is an effective approach to enhance the ionic conductivity.

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1. Introduction

As one of the most promising low-temperature energy-conversion devices, anion exchange membrane fuel cells (AEMFCs) have recently been revitalized by the promising progress in anion

exchange membranes (AEMs) in the latest past decades [1–4]. Though attractive, the performance of AEMFCs, currently using non-precious metal (oxide) catalysts or even platinum-based catalysts, is still much lower than that of the acid counterpart, proton exchange membrane fuel cells (PEMFCs). For example, the state-of-the-art performance of AEMFCs (1.0 A cm^{-2} @ 0.6 V) [5] is much lower than that of PEMFCs (2.3 A cm^{-2} @ 0.6 V) [6] in the open literature. The practical cell performance of AEMFCs is largely

* Corresponding author.

E-mail address: metzhao@ust.hk (T.S. Zhao).

restricted by the low ionic conductivity of AEMs. To address this issue, intensive researches on AEMs have been performed and some promising results have been achieved.

Borrowed from the theoretical calculation equation ($\sigma_{OH^-} = \mu_{OH^-} \cdot FC_{OH^-}$) in liquid solutions, the ionic conductivity (σ) is determined by the ionic mobility (μ) and the local ionic concentration (C), i.e., ion exchange capacity (IEC) in solid polymer electrolytes (SPEs). Hence, there are two approaches to increase the ionic conductivity. The first approach is to increase the IEC, responding to the number of the conductive groups tethered in the polymer backbones or side chains. While intuitive, this strategy is not as straightforward as it seems. Due to the hydrophilic properties of the functional groups (typically quaternary ammonium groups (QAs)), AEMs with a high IEC will cause a high water uptake, and in turn causes swelling in the AEMs or dissolution into the solvents, especially at elevated temperatures [7]. To address this issue, a cross-linking process is indispensable. The cross-linking process significantly suppresses the water uptake, stabilizing the AEMs with high IEC values even at elevated temperatures. To improve conductivity even further, several approaches have been reported recently such as by (self)cross-linking the AEMs with high IEC values [7], modifying the functional groups to other cationic groups [1], fabricating two cations on each grafted functional group [8] and resonance-stabilizing by phenylguanidinium functional groups [9,10]. However, most of the AEMs in development exhibit ionic conductivities in the range of 10^{-3} to 10^{-2} S cm^{-1} , allowing much room for the improvement for practical applications.

The second approach is to manipulate the microstructure of AEMs with a moderate IEC, so that the hydroxide ions are readily conducted with an improved effective mobility. Perfluorosulfonic acid (PSFA, typically Nafion) is known as a highly efficient proton conductor due to the broad and well-connected hydrophobic/hydrophilic phase separation [11]. The hydrophobic phase consisting of PTFE main chains contributes to the mechanical properties of the solid polymer electrolyte while the well-connected hydrophilic phase consisting of sulfonic acid groups contributes to the high proton conduction. However, in the development of AEMs, the wisdom in building nano-phase separated, and well-connected hydrated channels for hydroxide conduction has not been well recognized until recently.

Zhuang et al. [7,12] introduced long alkyl side-chains to quaternary ammonia polysulfone (QAPSF) with a moderated IEC. It was demonstrated that the introduction of hydrophobic side chains could drive the aggregation of the hydrophilic domains, thus increasing the local hydroxide concentration and enhancing the hydroxide hopping conduction. This microphase-separation structure in QAPSF promoted the hydroxide ion conduction efficiently. It demonstrated that the conductivity reached 0.11 S cm^{-1} at 80 °C, which was even higher than that of Nafion at the same temperature. Watanabe et al. [13] synthesized the quaternized aromatic multiblock copolymers with a well-developed hydrophobic/hydrophilic phase separation and interconnected ion transporting pathway for hydroxide conduction. The as-prepared AEMs exhibited a hydroxide ion conductivity of 0.144 S cm^{-1} at 80 °C, which represented the highest hydroxide conductivity so far. Li and Hickner [14–16] fabricated a series of quaternary ammonia poly(2,6-dimethyl-1,4-phenylene oxide) (QAPPO) containing long alkyl side chains pendant to the nitrogen-centered cation. The comb-shaped AEMs showed a well-defined microstructure, which was demonstrated to a dramatic enhancement in hydroxide conductivity and water uptake resistance. The highest ionic conductivity of ~ 0.043 S cm^{-1} was achieved at 20 °C for these comb-shaped AEMs. Although promising progress has been made, research on this microstructure separation to enhance the ionic conductivity is still in its initial stages, and the nanoscale morphology in the AEMs is

difficult to be precisely controlled.

In this work, the QAPPO was selected to tune the microstructure through a self-aggregating design, in which the hydrophobic long alkyl side-chains were selected to be grafted on the bromomethylated PPO (BrPPO) backbone. The two different types of hydrophobic side chains and the amount of hydrophobic side chains were meticulously tuned during the synthesis process. The synthesis route is presented in Scheme 1. The microphase-separated structures were detected by atomic force microscopy (AFM) and small angle X-ray scattering (SAXS). The ionic conductivities of these novel AEMs were determined by the two-probe AC impedance method. The alkaline stability test was performed in an accelerated test protocol. Finally, these AEMs were used to alkaline polymer electrolyte water electrolysis, demonstrating that these QAPPO-based AEMs with a high ionic conductivity and enhanced durability were a promising candidate for alkaline electrochemical conversion and storage systems.

2. Experimental

2.1. Materials

Butylamine (99.5%), 2,2,3,3,4,4,4-heptafluorobutylamine (7FBuA, 96%), N-bromosuccinimide (NBS), 2,2'-Azo-bis-isobutyronitrile (AIBN), trimethylamine (TMA) and potassium hydroxide (KOH) were purchased from Sigma–Aldrich. Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) with a molecular weight of 350,000 g mol^{-1} was obtained from SABIC Innovative Plastics (PPO6130). AIBN was twice recrystallized from methanol. The PGM-free Acta 3030 OER power catalyst and PGM-free Acta 4030 HER power catalyst were obtained from Acta S.p.A. The anode and cathode gas diffusion layers, nickel foam and carbon paper were purchased from Hohsen and E-TEK, respectively. All other chemical agents were used as-received unless otherwise noted.

2.2. Synthesis of bromomethylated PPO

The preparation process of the bromomethylated PPO (BrPPO) with different degrees of bromomethylation (DOB, x) was achieved by controlling the ratio between the PPO and NBS, as reported elsewhere [17]. Generally, PPO (40 mmol) was dissolved in 200 mL chlorobenzene at 50 °C to obtain a clear solution. The solution was then added into a three-neck flask equipped with a water-cooling condenser and heated in an oil bath at 145 °C while magnetically stirred. The reaction was held at this temperature for 24 h after a desired mole of NBS and 4 mmol AIBN were successively added. Once the reaction was complete, the mixture was cooled to room temperature. The resulting deep red solution was poured slowly into 1000 mL methanol to precipitate the brown polymer. The polymer was then filtrated, carefully rinsed with methanol several times, and subsequently dissolved in chloroform and re-precipitated in the hot methanol solution. The polymer was then dried overnight in a vacuum oven at 80 °C.

2.3. Synthesis of QAPPO, QAPPO-CH and QAPPO-CF

The dried BrPPO (2.0 g) was dissolved into DMF to form a 5 wt.% solution. Subsequently, butylamine with the desired mole ratio (y) was added dropwise with stirring at 40 °C for 5 h. After that, TMA with the mole ratio of $x(100-y)$ was then added. The solution was stirred at 40 °C for an additional 5 h, precipitated in methanol and dried under vacuum at 60 °C to obtain QAPPO-CH. BrPPO was grafted with 7FBuA and aminated by TMA with the same process to obtain QAPPO-CF. For the purpose of comparison, the ionomer solely aminated by TMA with a mole ratio of x was also prepared,

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