A novel guanidinium grafted poly(aryl ether sulfone) for high-performance hydroxide exchange membranes†

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A novel poly(aryl ether sulfone) ionomer containing hexaalkylguanidinium groups was synthesized, and membranes formed from this polymer displayed large ionic clusters, high hydroxide conductivity, and excellent solubility in low boiling point water-soluble solvents such as ethanol and methanol.

A transition to renewable and low-carbon forms of energy is being widely debated as a means of securing a sustainable future for mankind.[1] Fuel cells have the potential to provide clean and efficient energy sources for stationary, traction, and portable applications.[2] Of the several different types of fuel cells under development today, polymer electrolyte fuel cells (PEFCs) have been recognized as a potential future power source for zero-emission vehicles.[3] Polymer electrolyte membranes are one of the main components of PEFCs. Two types of solid polymer electrolyte have been studied in fuel cell research: proton exchange polymer membranes (PEMs) and hydroxide exchange polymer membranes (HEMs). Over the past decade, vast resources have been devoted to developing PEMs.[4] Although PEMs exhibit excellent chemical, mechanical, and thermal stability as well as high ionic conductivity, several disadvantages, such as slow anode kinetics, parasitic methanol crossover, and the requirement for expensive platinum-based catalysts, have obstructed the commercialization of proton exchange membrane fuel cells (PEMFCs).[5] To overcome these hurdles, HEMs were developed. Hydroxide exchange membrane fuel cells (HEMFCs) have numerous advantages over PEMFCs in terms of both cathode kinetics and ohmic polarization. The inherently faster kinetics of the oxygen reduction reaction in an alkaline fuel cell allow the use of non-noble and low-cost metal electrocatalysts, such as silver and nickel. Fuel oxidation is more facile in alkaline media than in acidic media.[6] In addition, the direction of hydroxide ion conduction opposes that of methanol crossover, thereby mitigating or possibly eliminating fuel crossover.[7]

Recently, Varcoe and co-workers reported the first example of metal cation-free alkaline membrane electrode assemblies for use in all-solid-state alkaline fuel cells with long-term performance stability.[8] The success of these assemblies has inspired increasing interest in HEMs. Commercially available anion exchange membranes are typically based on cross-linked polystyrene and are not very stable in alkaline environments. For the design of novel HEMs, aromatic ionomers are considered promising alternative materials for fuel cell applications due to their high thermal stability, excellent mechanical strength, and superior chemical resistance in acidic and alkaline conditions. To date, most HEMs have been constructed mainly from poly(aryl ether sulfone),[9] poly(phenylene),[10] poly(2,6-dimethyl-1,4-phenylene oxide),[11] radiation-grafted PVDF, ETFT, and FEP.[7b,12] Their development, however, has been hampered by the poor solubility and low hydroxide conductivity of the HEMs. One of the most desirable properties of an ionomer for use in a catalyst layer is excellent solubility in low boiling point water-soluble solvents, such as ethanol, because these solvents are easy and safe to handle, and they are removed during electrode preparation.[9a] Because most of the polymers used as HEMs were not soluble in ionomer form, their ability to form an efficient three-phase-boundary structure in the catalyst layer has been questionable, thereby limiting performance.[13] The most commonly used material for hydroxide exchange is a quaternary ammonium hydroxide containing-polymer that exhibits poor hydroxide conductivity, partly due to incomplete ionization of quaternary ammonium hydroxide.[10–12]

Hexaalkylguanidinium salts are used as ionic liquids due to their intrinsically useful properties, such as negligible vapor pressures, elevated thermal and chemical stabilities under thermal, basic, acidic, nucleophilic and oxidative conditions, and large electrochemical windows.[14] Furthermore, the pK_a of pentaalkylguanidine ($pK_a = 13.8$) is higher than that of trimethylamine ($pK_a = 10.8$), indicating that hexaalkylguanidinium hydroxide is a stronger base than quaternary ammonium hydroxide.[15] Due to their strongly basic character, guanidines are considered superbases.[16] Their high alkalinity yields a high concentration of mobile hydroxide ions. More recently, we have prepared novel HEMs that contain hexaalkylguanidinium functionalities exhibiting high hydroxide conductivity and outstanding alkaline stability.[17] They were prepared by chloromethylation of the polysulfone, followed by reaction with 1,1,2,3,3-pentamethylguanidine to form hexaalkylguanidinium groups. However, the chloromethylation reaction is usually restricted due to the use of a toxic reagent, chloromethyl methyl ether[18] and the lack of precise control over the degree and location of functionalization.[6,19]

In the present study, hexaalkylguanidinium hydroxide was attached to poly(aryl ether sulfone), abbreviated PES-G-OH. The synthesis of this polymer is illustrated in Scheme 1. We developed a novel side chain type monomer (PPH-MPDA), 3,3-bis(4-hydroxyphenyl)-2-(3-(methylamino)propyl)isoindolin-1-one, which contained an aliphatic diamine group. The aromatic poly(aryl ether sulfone) with pendant diamine

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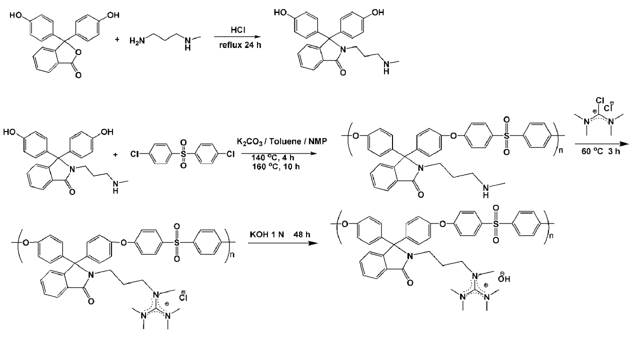

Scheme 1 Synthesis of poly(aryl ether sulfone) containing hexaalkylguanidinium groups (PES-G-OH).

groups (PES-A) was obtained by reacting PPH-MPDA with 4,4′-dichlorodiphenyl sulfone in the presence of K_2CO_3 as a base and catalyst in NMP. Using typical polymerization conditions, the aprotic dipolar reaction system could be dehydrated using toluene until a final polymerization temperature of 160–165 °C was reached. Careful control of the polymerization temperature (160–165 °C) was required to avoid cross-linking. The hexaalkylguanidinium hydroxide-containing polymer (PES-G-OH) was prepared by the reaction of Vilsmeier salt and the diamine groups in PES-A, followed by hydroxide ion exchange. The structure of the polymer was analyzed by ^{1}H and ^{13}C NMR analyses to examine the change in molecular structure during the synthetic process (see ESI†). The peaks at 2.10 and 2.16 ppm were assigned to the chemical shifts of protons on, respectively, the methyl or methylene groups attached to the nitrogen atom in PES-A. After the reaction, these peaks disappeared and new peaks emerged between 2.65 and 2.90 ppm that were assigned to the proton of the hexaalkylguanidinium hydroxide. The ^{13}C NMR spectra also verified the structure of PES-G-OH. In addition to the emergence of new peaks between 46.97 and 35.63 ppm, the peak at 162.46 ppm, which corresponded to the carbon atom at the centre of the hexaalkylguanidinium group, was observed. ^{1}H and ^{13}C NMR revealed that the reaction proceeded quantitatively.

Recently, Hickner *et al.* reported a process in which the polymer converted to its ionic form in solution and formed a membrane, and they demonstrated that the membrane promoted ionic aggregation and, thus, higher conductivity.[20] In such a process, solubility is a key property of ionomers used to form HEMs. The ionomer described here exhibited outstanding solubility in polar aprotic solvents, such as DMF, DMAc, DMSO, and NMP. Membranes were prepared by dissolving the ionomers in NMP followed by casting on a levelled Teflon sheet. Above all, the PES-G-OH ionomer exhibited excellent solubility in low boiling point water-soluble solvents (Table S1), such as ethanol and methanol, which was similar to the solubility of quaternary phosphonium-containing polymers reported by Yan and co-workers.[9a] The PES-G-OH ionomer was insoluble in pure water, even at 100 °C, suggesting that it could be used in the catalyst layer without incurring loss due to dissolution.

The water uptake, swelling ratio, and ion exchange capacity (IEC) of the membrane are reported in Table S2. At 60 °C, PES-G-OH membrane exhibited a moderate water uptake (35.8% for PES-G-OH) and swelling ratio (15.2% for PES-G-OH).

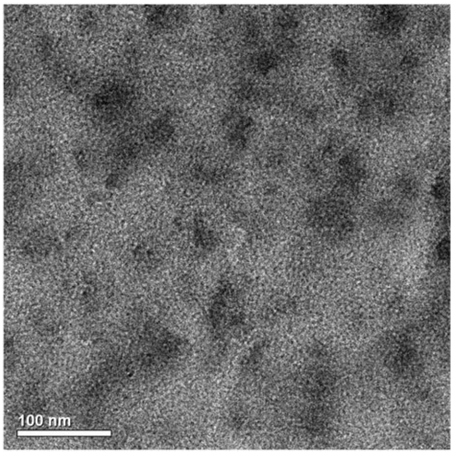

Fig. 1 TEM image of Pd^{2+}-stained membrane: PES-G-OH, IEC = 1.39 meq/g.

Transmission electron microscopy (TEM) analyses were performed in the palladium form (Fig. 1). In the TEM image, the ionic domains appear as a dark area due to their affinity with $PdCl_4^{2-}$ anion, and the white areas represent the hydrophobic regions of the polymer nanostructure.[9b] As can be seen in Fig. 1, ionic clusters of PES-G-OH, recognized as dark areas (*ca.* 40–50 nm in diameter) in the TEM images, could be clearly observed. The average size of the ionic regions in the PES-G-OH membrane was markedly larger than that in the membranes containing quaternary ammonium groups, reported by Zhuang's group,[9b] which displayed ionic clusters tens of nanometres in size. The excellent phase-separated morphology of the PES-G-OH membrane was attributed to two factors: bulky volume and strong hydrophilicity of the hexaalkylguanidinium groups.

Perhaps the most important property of membranes employed in HEMFC applications is the hydroxide conductivity. Fig. 2 shows the dependence of membrane hydroxide conductivity on temperature over the range 15–60 °C. For comparison, the conductivity of Nafion 117 was also measured under the same conditions. By way of comparison, Coates'

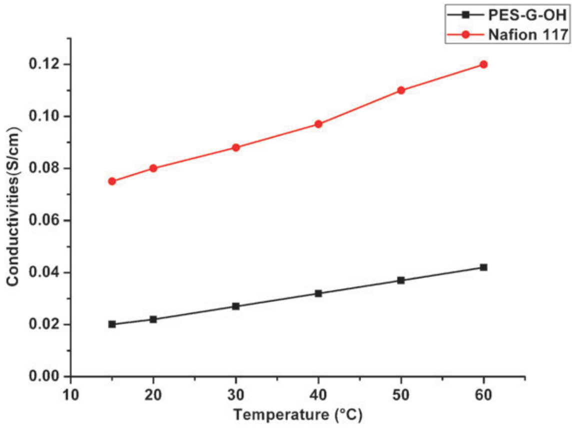

Fig. 2 Temperature dependence of the hydroxide ion conductivity of the membranes.

HEMs (IEC = 1.40 meq/g) exhibited 0.028 S cm^{-1} at 50 °C.[21] We recently reported tetraalkylammonium-functionalized HEM (IEC = 1.47 meq/g) conductivities of 0.018 S cm^{-1} at 60 °C.[9d] The hydroxide conductivities of the PES-G-OH membrane (IEC = 1.39 meq/g) were 0.037 S cm^{-1} at 50 °C, and 0.42 S cm^{-1} at 60 °C, respectively. The PES-G-OH membrane showed a hydroxide conductivity that was much higher than those of the tetraalkylammonium-functionalized HEMs mentioned above. This phenomenon was attributed to the strong basicity of the hexaalkylguanidinium hydroxide which provided a high concentration of mobile hydroxide ions.

The thermal stability of the PES-G-OH membrane (TGA curve) is reported in Fig S3. The PES-G-OH polymer showed a 5% weight loss at 327 °C, which was 60 °C higher than that of membranes containing quaternary ammonium hydroxide groups (360 °C).[9d] As expected, the PES-G-OH membrane exhibited a higher stability than the tetraalkylammonium-functionalized membrane. In addition to excellent thermal stability, PES-G-OH exhibited outstanding alkaline stability. PES-G-OH membrane maintained its ionic conductivity even after immersion in 10 M NaOH solution at 25 °C and 2 M NaOH solution at 80 °C for 24 h (see Table S3 in the Supporting Information). By contrast, the commercially available AMI-7001S, MA-3475 and AMB-SS anion exchange membranes soaked in 1 M KOH underwent severe color change, which was observed in as little as 5 min.[22] This phenomenon has been attributed to deterioration of the chemical structure.[22] No change in color for PES-G-OH membrane was observed during any soaking period, suggesting negligible chemical deterioration. And the PES-G-OH membrane maintained its ionic conductivity after immersion in either DI water or 1 M NaOH for one week at room temperature, indicating good alkaline stability.

In summary, a novel side chain-type poly(aryl ether sulfone) containing hexaalkylguanidinium groups was prepared *via* typical nucleophilic substitution polymerization followed by the reaction of the diamine groups with Vilsmeier salt. PES-G-OH displayed excellent solubility in some low boiling point water-soluble solvents, methanol and ethanol, and outstanding stability. Enhanced phase separation and high hydroxide conductivity were observed, which constituted improvements over conventional quaternary ammonium hydroxide-containing polymers.

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Notes and references

1 D. A. J. Rand and R. M. Dell, *Hydrogen Energy Challenges and Prospects*, RSC, Cambridge, UK, 2008.
2 M. Ünlü, J. F. Zhou and P. A. Kohl, *J. Phys. Chem. C*, 2009, **113**, 11416–11423.
3 R. Bashyam and P. Zelenay, *Nature*, 2006, **443**, 63–66.
4 (*a*) K. Miyatake, T. Shimura, T. Mikami and M. Watanabe, *Chem. Commun.*, 2009, 6403–6405; (*b*) S. Seesukphronrarak and A. Ohira, *Chem. Commun.*, 2009, 4744–4746.
5 (*a*) X. Kong, K. Wadhwa, J. G. Verkade and K. Schmidt-Rohr, *Macromolecules*, 2009, **42**, 1659–1664; (*b*) Y. Wan, B. Peppley, K. A. M. Creber and V. T. Bui, *J. Power Sources*, 2010, **354**, 23–31.
6 G. Wang, Y. Weng, D. Chu, R. Chen and D. Xie, *J. Membr. Sci.*, 2009, **332**, 63–68.
7 (*a*) N. J. Robertson, H. A. Kostalik IV, T. J. Clark, P. F. Mutolo, H. D. Abruna and G. W. Coates, *J. Am. Chem. Soc.*, 2010, **132**, 3400–3404; (*b*) J. R. Varcoe, R. C. T. Slade, E. L. H. Yee, S. D. Poynton, D. J. Driscoll and D. C. Apperley, *Chem. Mater.*, 2007, **19**, 2686–2693.
8 J. R. Varcoe, R. C. T. Slade and E. L. H. Yee, *Chem. Commun.*, 2006, 1428–1429.
9 (*a*) S. Gu, R. Cai, T. Luo, Z. Chen, M. Sun, Y. Liu, G. He and Y. Yan, *Angew. Chem., Int. Ed.*, 2009, **48**, 6499–6502; (*b*) J. Pan, S. Lu, Y. Li, A. Huang, L. Zhuang and J. Lu, *Adv. Funct. Mater.*, 2010, **20**, 312–319; (*c*) S. Lu, J. Pan, A. Huang, L. Zhuang and J. Lu, *Proc. Natl. Acad. Sci. U. S. A.*, 2008, **105**, 20611–20614; (*d*) J. Wang, Z. Zhao, F. Gong, S. Li and S. Zhang, *Macromolecules*, 2009, **42**, 8711–8717.
10 (*a*) M. R. Hibbs, C. H. Fujimoto and C. J. Cornelius, *Macromolecules*, 2009, **42**, 8316–8321; (*b*) E. E. Switzer, T. S. Olson, A. K. Datye, P. Atanassov, M. R. Hibbs, C. Fujimoto and C. J. Cornelius, *Electrochim. Acta*, 2010, **55**, 3404–3408.
11 (*a*) Y. Wu, C. Wu, J. R. Varcoe, S. D. Poynton, T. Xu and Y. Fu, *J. Power Sources*, 2010, **195**, 3069–3076; (*b*) L. Wu and T. Xu, *J. Membr. Sci.*, 2008, **322**, 286–292; (*c*) Y. Wu, C. Wu, T. Xu, X. Lin and Y. Fu, *J. Membr. Sci.*, 2009, **338**, 51–60.
12 (*a*) R. C. T. Slade and J. R. Varcoe, *Solid State Ionics*, 2005, **176**, 585–597; (*b*) T. N. Danks, R. C. T. Slade and J. R. Varcoe, *J. Mater. Chem.*, 2002, **12**, 3371–3373.
13 (*a*) G. Wang, Y. Weng, D. Chu, D. Xie and R. Chen, *J. Membr. Sci.*, 2009, **326**, 4–8; (*b*) M. R. Hibbs, M. A. Hickner, T. M. Alam, S. K. McIntyre, C. H. Fujimoto and C. J. Cornelius, *Chem. Mater.*, 2008, **20**, 2566–2573; (*c*) J. S. Park, S. H. Park, S. D. Yim, Y. G. Yoon, W. Y. Lee and C. S. Kim, *J. Power Sources*, 2008, **178**, 620–626.
14 N. M. M. Mateus, L. C. Branco, N. M. T. Lourenço and C. A. M. Afonso, *Green Chem.*, 2003, **5**, 347–352.
15 R. S. Blackburn, A. Harvey, L. L. Kettle, J. D. Payne and S. J. Russell, *Langmuir*, 2006, **22**, 5636–5644.
16 T. Isobe, K. Fukuda and T. Ishikawa, *J. Org. Chem.*, 2000, **65**, 7770–7773.
17 J. Wang, S. Li and S. Zhang, *Macromolecules*, 2010, **43**, 3890–3896.
18 (*a*) A. Blair and N. Kazerouni, *Cancer, Causes Control*, 1997, **8**, 473–490; (*b*) S. Laskin, M. Kusschner, R. T. Drew, V. P. Capiello and N. Nelson, *Arch. Environ. Health*, 1971, **23**, 135–142.
19 M. Tanaka, M. Koike, K. Miyatake and M. Watanabe, *Macromolecules*, 2010, **43**, 2657–2659.
20 J. Yan and M. A. Hickner, *Macromolecules*, 2010, **43**, 2349–2356.
21 T. J. Clark, N. J. Robertson, H. A. Kostalik IV, E. B. Lobkovsky, P. F. Mutolo, H. D. Abruna and G. W. Coates, *J. Am. Chem. Soc.*, 2009, **131**, 12888–12889.
22 J. A. Vega, C. Chartier and W. E. Mustain, *J. Power Sources*, 2010, **195**, 7176–7180.