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Guanidinium-Functionalized Anion Exchange Polymer Electrolytes via Activated Fluorophenyl-Amine Reaction

Dae Sik Kim,[†] Andrea Labouriau,[‡] Michael D. Guiver,[§] and Yu Seung Kim*,[†]

[†]Materials Physics and Applications, Sensors and Electrochemical Devices Group and [‡]Materials Science and Technology Polymers and Coatings Group, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, United States

[§]Institute for Chemical Process and Environmental Technology, National Research Council, 1200 Montreal Road, Ottawa, Ontario K1A 0R6, Canada

S Supporting Information

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Renewed interest has grown in the development of alkaline membrane fuel cells (AMFCs) in recent years, primarily because the efficiency of the oxygen reduction reaction of electrocatalysts in alkaline environment is likely greater than in acidic conditions and therefore, expensive platinum-based catalysts can be replaced with inexpensive ones such as nickel, silver and carbon.[1−3] Quaternary ammonium-tethered anion exchange polymer electrolytes[4−9] have been the most extensively studied; nevertheless degradation of alkyl ammonium-based polymer electrolytes occurs under high pH conditions via (i) Hoffmann elimination (E_2), (ii) nucleophilic substitution (S_N2),[10] or (iii) ylide formation.[11] Although the E_2 reaction can be circumvented by avoiding a coplanar arrangement of β-hydrogen and nitrogen or by synthesizing β-hydrogen-absent quaternary ammoniums, most of the alkyl ammonium-functionalized polymers still have not realized sufficient stability because of the S_N2 reaction. In the S_N2 reaction, hydroxide ions attack the α-carbon of the ammonium cations. The extent of polymer degradation via the S_N2 reaction may be reduced by replacing alkyl ammonium with bulky cations such as guanidinium or phosphonium, which stabilize the α-carbon−nitrogen bond by charge delocalization of the cations.[12] Degradation through the ylide pathway starts with hydroxide ion attack on a CH_3 proton and produces a water molecule along with an ylide intermediate ($N(CH_3)_3{}^+CH_2{}^-$).[11]

Most cation-functionalized polymer electrolytes have been prepared via chloromethylation (or bromination of methyl groups) and subsequent cationization of the halomethyl group.[7,8,13,14] However, benzyl guanidiniums were reported to undergo faster degradation than phenyl guanidiniums due to the nucleophilic attack by hydroxide ion at the benzylic cation.[15] Furthermore, the degradation of benzyl ammonium through ylide formation and subsequent rearrangement reactions may limit the lifetime of the polymers.[16] We report herein a controlled and efficient method to incorporate bulky guanidinium cations into polymers using activated aromatic fluorine atoms, followed by methylation, thereby producing phenyl-guanidinium; this avoids the halomethylation process that leads to benzyl-cation formation. The electrochemical properties and stability of the phenyl-guanidinium are investigated under ex situ and AMFC operating conditions.

Scheme 1 shows the synthetic procedure to prepare phenyl-guanidinium functionalized poly(arylene ether sulfone). The 1,1-bis(4-hydroxyphenyl)-1-(4-((4-fluorophenyl)-thio) phenyl-2,2,2-trifluoroethane) (3FBPT) monomer was synthesized by the nucleophilic displacement of activated fluorine on 4-fluoro-2,2,2-trifluoroacetophenone (F3FAP) by 4-fluorothiophenol (FTP), followed by a phenol condensation reaction.[17,18] Poly(arylene ether sulfone) containing pendant 4-fluorophenyl sulfide groups (PAES-S) was synthesized by nucleophilic aromatic substitution (S_NAr) polycondensation using 3FBPT and 4,4′-difluorodiphenylsulfone (DFS). The pendant 4-fluorophenyl groups of the polymer were activated by oxidizing sulfide to sulfone with hydrogen peroxide in formic acid polymer suspension to give PAES-SO_2. The molecular weight of PAES-SO_2 was 50.2 kg/mol (M_n) and 75.6 kg/mol (M_w) (PDI = 1.51).[19] The excellent reactivity of the fluorine atom on the pendant group was demonstrated by the reaction of PAES-SO_2 with 1,1,3,3-tetramethylguanidine (TMG) at 130 °C in DMAc. In this PAES-TMG system, it is unnecessary to prepare a pentamethyl guanidinium, since commercially available TMG reacts directly with the activated fluorine of PAES-SO_2. The PAES-TMG polymer was converted to the methylated polymer (M-PAES-TMG) by reaction with dimethyl sulfate (DMS) at 90 °C for 12 h.

The ^1H NMR spectra of the PAES-S and PAES-SO_2 polymers show that the ortho sulfonyl protons (H-2 and H-3) appear at higher frequencies than the respective thioether protons because of the deshielding effect of the sulfone groups, whereas the electron-rich ortho ether linkage protons appear at lower frequencies (see Figure S1 in the Supporting Information). The ^1H NMR spectra of both PAES-TMG and M-PAES-TMG are shown in Figure 1. The $-CH_3$ signal of PAES-TMG was observed at δ 2.5−2.7 ppm. The yield of TMG attachment was calculated from ^1H NMR. The integration ratio of H (6.5−8.3 ppm, benzene ring, 24H) to H (2.5−2.7 ppm, TMG, 12H) from Figure 1 is 2:0.99 (theoretical ratio is 2:1), indicating that the yield of TMG attachment is nearly 100%. This result is in good agreement with the yield calculated from ^{19}F NMR by the integration ratio of fluorine of polymer before and after fluorophenyl-amine reaction (see Figure S2 in the Supporting Information). After methylation, the $-CH_3$ signal of PAES-TMG was shifted to higher frequencies (δ 3.0−3.1) because of deshielding from the quaternary nitrogen atom. An enhanced $-CH_3$ signal of

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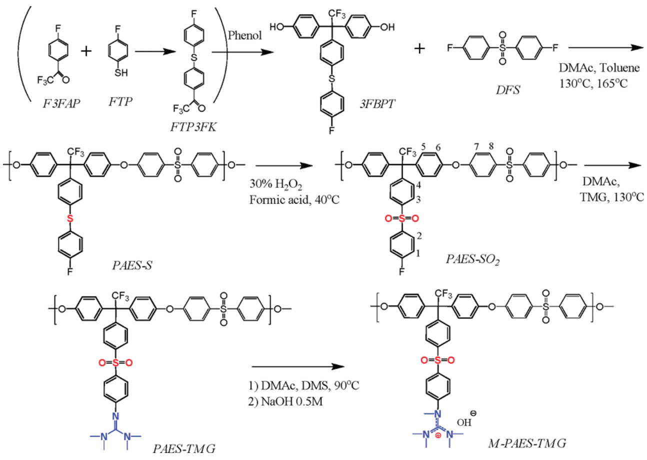
Scheme 1. Synthesis of Phenyl-guanidinium-Functionalized Poly(arylene ether sulfone)



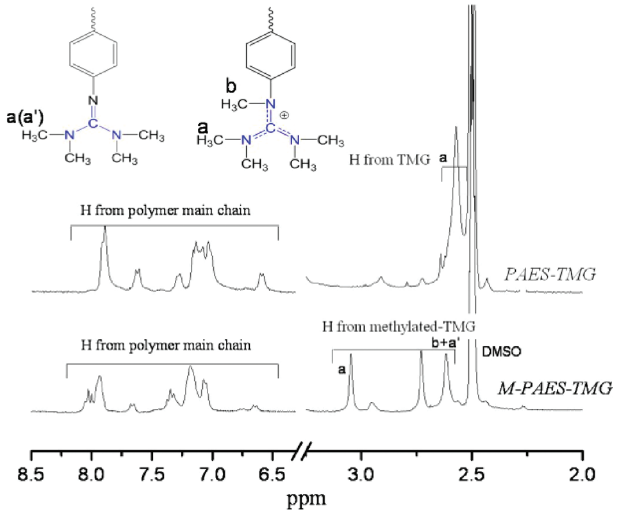


Figure 1. ^1H NMR spectra of (a) PAES-S and PAES-SO_2, (b) PAES-TMG and M-PAES-TMG.

M-PAES-TMG was observed at δ 2.6–2.8 after methylation, which includes the $-CH_3$ groups of M-PAES-TMG as well as nonmethylated PAES-TMG. The methylation degree was calculated from the integration ratio of H (benzene ring, 24H) to H (methyl groups, 15H) of PAES-TMG. The theoretical integration ratio around δ 6.5–8.3 to δ 2.55–3.1 of M-PAES-TMG is 1.6:1 and the signal integration ratio (Figure 1) was close to 1.6:0.85 (i.e., the methylation degree: 85%). This gives a calculated ion exchange capacity (IEC) of 1.03 mequiv/g for M-PAES-TMG. Complete methylation of the phenyl-TMG was probably inhibited by the high basicity of TMG. The methylation using conventional CH3I was less effective and produced <60% yield (see Figure S3 in the Supporting Information). The conjugation of phenyl-pentamethyl guanidinium after methylation was confirmed by FT-IR: the C═N absorption at 1547 cm^{-1} decreased, while the CN_3 conjugation absorption (1627, 1537 cm^{-1}) emerged (see Figure S3 in the Supporting Information).

The anionic conductivity was measured in two different conditions (hydroxide- and bicarbonate-rich environments). The hydroxide-rich environment was achieved by immersion in 0.5 M sodium hydroxide aqueous solution for 48 h, subsequent boiling deionized water and purging N_2 gas in a temperature/humidity control chamber while the bicarbonate-rich environment was obtained after 24 h exposure of deionized water to ambient air. Figure 2 showed that the conductivity under a hydroxide-rich environment was about 2-fold greater than the conductivity under a bicarbonate-rich environment and the conductivities increased linearly with temperature. Anion conductivity of M-PAES-TMG was also measured in NaOH and K_2CO_3 solution as a function of NaOH and K_2CO_3 concentration (see Figure S4 in the Supporting Information). In the experimental concentration range (0.01–0.1 N), the conductivity in NaOH solution is about 2-fold greater than the conductivity in K_2CO_3 solution.[8] Considering the infinite diffusion coefficient of hydroxide ion is 3.7 and 5.8 times higher than those of carbonate and bicarbonate ions, respectively,[8,20] this result suggests other factors such as cation–anion interaction or insufficient equilibrium time[8] may also impact the anion mobility. The water uptake of M-PAES-TMG was only 10 wt % at 30 °C, which was notably lower than that of benzyl-trialkyl ammonium functionalized polymers. The reported water uptake of benzyl-trialkyl ammonium functionalized polymers with similar conductivities (ca. 12 mS/cm) was ~60 wt % when measured under the same conditions.[5,7]

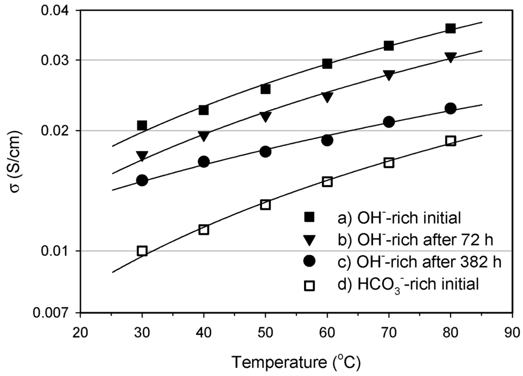


Figure 2. Anion conductivity (σ) of M-PAES-TMG as a function of temperature (a) before stability test, (b) after 72 h life test, (c) after 382 h life test under hydroxide-rich environment, and (d) before stability test under bicarbonate-rich environment.

The stability of M-PAES-TMG was evaluated by immersion of the membrane into 0.5 M NaOH solution at 80 °C. The anionic conductivity of M-PAES-TMG slightly decreased from 36 to 31 mS/cm after 72 h (14%) and further decreased to 23 mS/cm after 382 h (36%). The FT-IR results exhibited a gradual decrease in the CN_3 conjugation band, while a new absorption at 1673 cm^{-1} in FT-IR and 2.88 ppm in ^1H NMR appeared during the stability test (see Figure S5 in the Supporting Information). The IEC of M-PAES-TMG calculated from ^1H NMR also decreased from 1.03 to 0.77 mequiv/g after 382 h (25%). Since the strongly electron-withdrawing sulfone group is connected to the phenyl-guanidinium, the electron density of the central carbon of the guanidinium reduces and its susceptibility to S_N2 reaction increases (see Scheme S1 in the Supporting Information).[21] Nevertheless, there is no evident degradation on the α-carbon–nitrogen bond found in other alkyl ammonium functionalized polymers.

The AMFCs using M-PAES-TMG as electrode ionomers drew significant currents with platinum catalysts under H_2/O_2 conditions (*ca.* the peak power density at 80 °C is ~200 mW/cm^2, see Figure S6 in the Supporting Information). More importantly, the AMFC using the M-PAES-TMG ionomer exhibited good stability

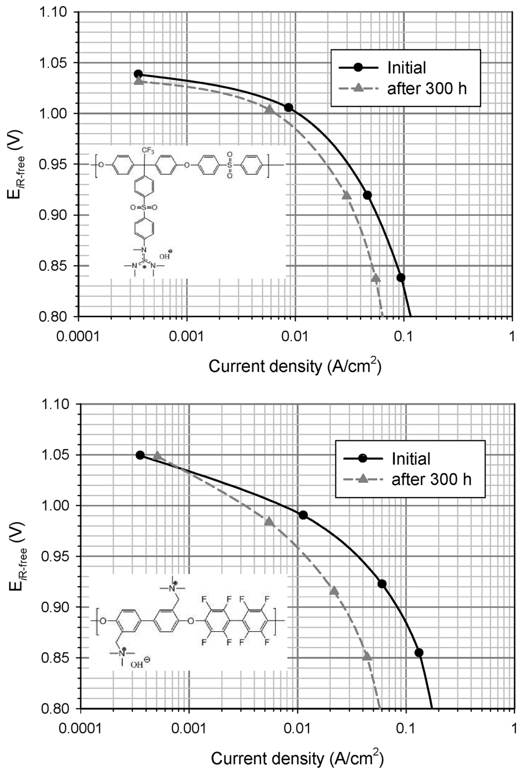


Figure 3. *i*R-free H_2/O_2 polarization curves of AMFCs using M-PAES-TMG and benzyl-trimethyl ammonium functionalized poly(arylene ether) in the catalyst layers before and after 300 h lifetime test. Measurements were taken at T_{cell} = 60 °C under fully humidified conditions (60 and 70 °C due point for anode and cathode, respectively, reactant backpressure at 30 psi).

as we compared the stability with benzyl-trimethyl ammonium functionalized control (see Scheme S1 in the Supporting Information). Figure 3 compares the Tafel-slope change at high voltage during the test in order to quantify the ionomer stability, with the assumption that the degradation of high-loading platinum black catalyst is negligible. The Tafel-slope at 0.96 V of MEA using M-PAES-TMG as electrode ionomer increased only 0.7 mV/decade after 300 h (2 μV/dec h), whereas the Tafel-slope of the MEA using benzyl-trimethyl-ammonium-tethered poly(arylene ether) ionomer increased 20.7 mV/decade (69 μV/dec h). Relatively insignificant degradation for both ionomers in the fuel cell lifetime test is possibly attributed to the absence of NaOH solution and lower operating temperature.

In summary, we have demonstrated a new synthetic method for the incorporation of bulky guanidinium functional groups into a polymer using activated fluorophenyl-amine reaction. The reaction produced a phenyl guanidinium cation functionalized polymer which exhibited highly efficient anion conductivity and promising stability in high pH conditions. The AMFC using the polymer as electrode ionomer exhibited superior stability to traditional benzyl-trimethyl functionalized polymer, indicating that the new synthetic routes can be effectively used for preparing new cation-containing polymer electrolytes.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details, spectroscopic data, polarization curves, and proposed degradation mechanism of this material are available free of charge via Internet at http://pubs.acs.org/.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: yskim@lanl.gov.

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■ REFERENCES

(1) Varcoe, J R.; Slade, R. C. T. *Fuel Cells* **2005**, *5*, 187.

(2) Spendelow, J. S.; Wieckowski, A. *Phys. Chem. Chem. Phys* **2007**, *9*, 2654–2675.

(3) Lu, S.; Pan, J.; Hunag, A.; Zhung, L.; Lu, J. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 20611–20614.

(4) Varcoe, J. R.; Slade, R. T. C.; Yee, E. L.; Poynton, S. D.; Driscoll, D. J.; Apperley, D. C. *Chem. Mater.* **2007**, *19*, 2686–2693.

(5) Hibbs, M. R.; Hickner, M. A.; Alam, T. M.; McIntyre, S. K.; Fujimoto, C. H.; Cornelius, C. J. *Chem. Mater.* **2008**, *20*, 2566–2573.

(6) Pan, J.; Lu, S.; Li, Y.; Huang, A.; Zhuang, L.; Lu, J. *Adv. Funct. Mater* **2010**, *20*, 312–319.

(7) Tanaka, M.; Koike, M.; Miyatake, K.; Watanabe, M. *Macromolecules* **2010**, *43*, 2657–2659.

(8) Yan, J.; Hickner, M. A. *Macromolecules* **2010**, *43*, 2349–2356.

(9) Robertson, N. J.; Kostalik, H. A., IV; Clark, J. T.; Mutolo, P. F.; Abruna, H. D.; Coates, G. W. *J. Am. Chem. Soc.* **2010**, *132*, 3400–3404.

(10) Bauer, B.; Strathmann, H.; Effenberger, F. *Desalination* **1990**, *79*, 125–144.

(11) Chempath, S.; Einsla, B. R.; Pratt, L. R.; Macomber, C. S.; Boncella, J. M.; Rau, J. A.; Pivovar, B. S. *J. Phys. Chem. C* **2008**, *112*, 3179–3182.

(12) (a) Pivovar, B. S.; Thorn, D. L. U.S. Patent 7 439 275, 2008. (b) Pivovar, B. S.; Thorn, D. L. U.S. Patent 7 846 980, 2010.

(13) (a) Wang, J.; Li, S.; Zhang, S. *Macromolecules* **2010**, *43*, 3890–3896. (b) Zhang, W.; Li, S; Zhang, S. *Chem. Commun.* **2010**, *46*, 7495–7497.

(14) Gu, S.; Cai, R.; Luo, T.; Chen, Z.; Sun, M.; He, G.; Yan, Y. *Angew. Chem., Int. Ed.* **2009**, *121*, 6621–6624.

(15) Hibbs, M.; Fujimoto, C.; Lambert, T.; Kim, D. S.; Kim, Y. S. North American Membrane Society (NAMS) meeting 2011, June 4—8, 2011, Las Vegas.

(16) Chempath, S.; Boncella, J. M.; Pratt, L. R.; Henson, N.; Pivovar, B. S. *J. Phys. Chem. C* **2010**, *114*, 11977–11983.

(17) Li, Z.; Ding, J.; Robertson, G. P.; Guiver, M. D. *Macromolecules* **2006**, *39*, 6990–6996.

(18) Kim, D. S.; Robertson, G. P.; Guiver, M. D. *Macromolecules* **2008**, *41*, 2126–2134.

(19) Zhou, J.; Unlu, M.; Anestis-Richard, I.; Kohl, P. A. *J. Membr. Sci.* **2010**, *350*, 286–292.

(20) Cussler, E. L. *Diffusion, Mass Transfer in Fluid Systems*, 2nd ed.; Cambridge University Press: Cambridge, U.K., 1997.

(21) Huczynski, A.; Janczak, J.; Brzezinski, B. *J. Mol. Struct.* **2010**, *967*, 65–71.