Supporting Information

Resonance Stabilized Perfluorinated Ionomers for Alkaline Membrane Fuel Cells

Dae Sik Kim,[a] Cy H. Fujimoto,[b] Michael R. Hibbs,[b] Andrea Labouriau,[a] Yoong-Kee Choe,[c] and Yu Seung Kim*[a]

1. FT-IR Spectrum of 1,1,3,3 Tetramethyl Guanidinium

1,1,3,3 tetramethylguanidine (TMG) (Acros Organics) was dissolved in water (1 M). A drop of this solution was deposited and dried on an IR sample cartridge to measure FT-IR. Resonance stabilized single CN_3 peak appeared at 1596 cm^{-1}.

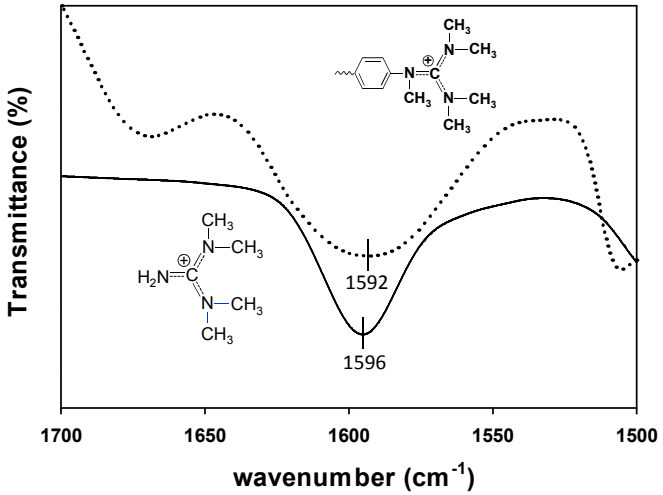

Figure S1. FT-IR Spectrum of 1,1,3,3 Tetramethyl Guanidinium (solid line) and Phenyl Pentamethyl Guanidinium (dotted line).

2. ^{1}H-NMR of M-Nafion-FA-TMG

Figure S2 shows the ^{1}H-NMR of M-Nafion-FA-TMG. TMG attachment and methylation yields were calculated from the integration ratio of protons of amide group (4.25 ppm, 1H), guanidinium (3.1-3.2 ppm-TMG, 12H), and methyl group (2.8-2.9 ppm, 3H).

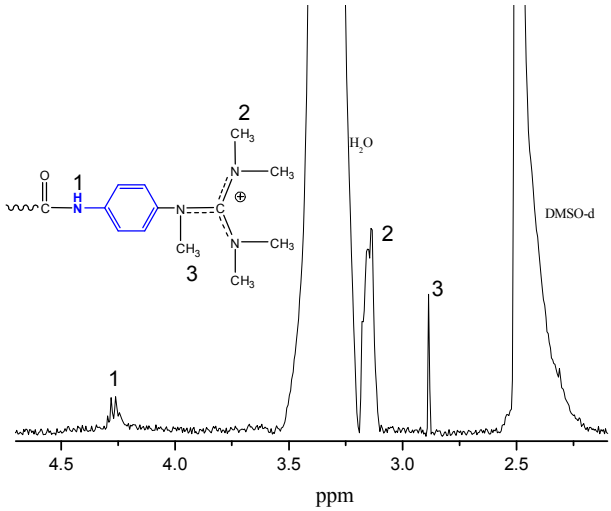

Figure S2. ^{1}H-NMR of M-Nafion-FA-TMG

3. ^{13}C-NMR of M-Nafion-TMG before and after NaOH treatment (0.5 M NaOH for 24 h)

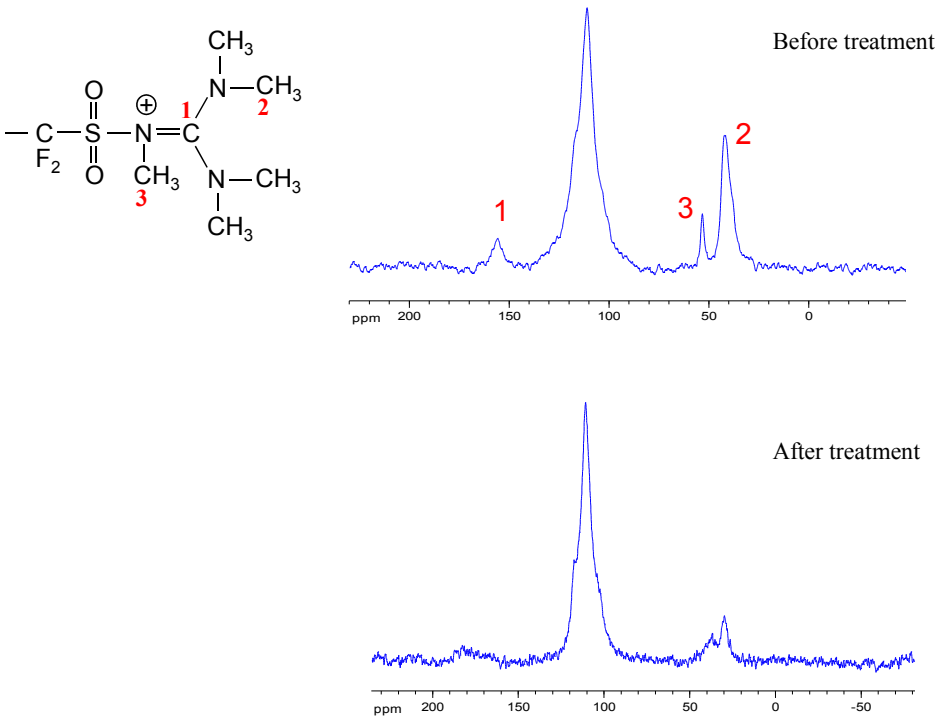

Figure S3. ^{13}C-NMR of M-Nafion-TMG before and after NaOH treatment

4. Barrier energy comparison of central carbon degradation for sulfone- and phenyl-guanidinium.

The central carbon degradation of sulfone- and phenyl-guanidinium is compared. The energy barrier of sulfone guanidinium degradation is 2.0 kcal/mol while corresponding value of phenyl guanidinium is 23.8 kcal/mol, indicating better stability of phenyl guanidinium with respect to the attack of OH^-. The degradation of sulfone guanidinium may occur in a step-wise manner, while that of phenyl guanidinium occurs in a concerted fashion. In reactant state, the bond length of C-N_L in M-Nafion-FA-TMG is computed to be 1.47 Å while that of M-Nafion-TMG is computed to be 1.53 Å, suggesting the more robust nature of the former.

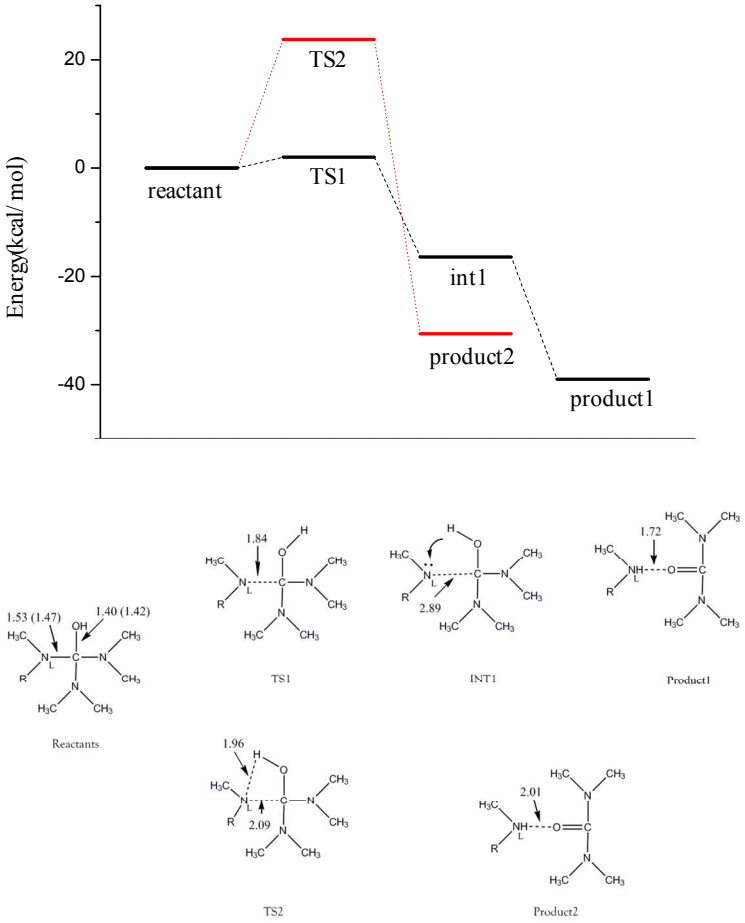

Figure S4. Energy profiles of the guanidinium degradation reactions caused by OH^-. The redline corresponds to the profile for phenyl guanidinium. Molecular structures of stationary points along the reaction coordinate. Some geometrical parameters [distances in Å] are shown. Given in parenthesis are values of phenyl guanidinium.