Electronic Supplementary Material (ESI) for Journal of Materials Chemistry
This journal is © The Royal Society of Chemistry 2011

SUPPORTING INFORMATION

A New Graphene-modified Protic Ionic Liquid-based Composite Membrane for Solid Polymer Electrolytes

Yun-Sheng Ye[a], Chi-Yung Tseng[a], Wei-Chung Shen[a], Jing-Shiuan Wang[a], Kuan-Jung Chen[a], Meng-Yao Cheng[a], John Rick[a], Yao-Jheng Huang[b], Feng-Chih Chang[b] and Bing-Joe Hwang[a]*

[a] Chemical Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan.
CORRESPONDING AUTHRO E-mail ADDRESS: bjh@mail.ntust.edu.tw

[b] Institute of Applied Chemistry, National Chiao-Tung University, Hsin-Chu, Taiwan.

S1. Experimental Section

S1.1. Materials

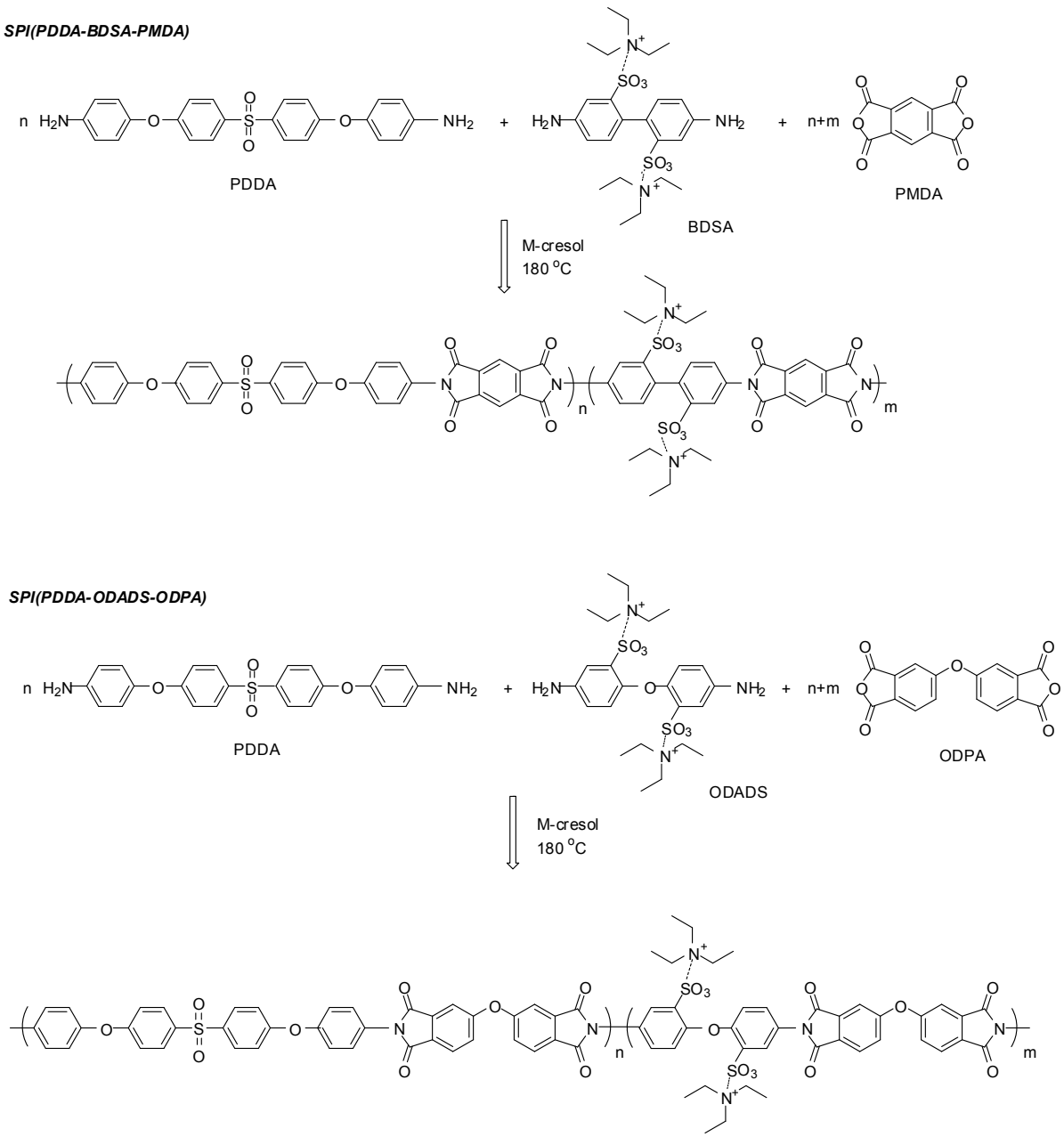
Triethylamine (TEA) (Aldrich), acetic anhydride (Acros), 2,2'-Benzidinesulfonic acid (BDSA) (Tokyo Kasei), m-Cresol (Wako Chem.), lithium bis(trifluoromethylsulfonyl) amide (Li^+NTFSI^-) (Acros), sodium tetrafluoroborate ($Na^+BF_4^-$) (Aldrich), dimethyl sulfoxide (DMSO) (Acros), dimethylformamide (DMF) (Acros), propylene carbonate (PC) (Acros) and acetonitrile (AN) (Acros) were used as received. Pyromellitic dianhydride (PMDA) (Aldrich), 4,4′-(1,3-Phenylenedioxy)dianiline (PDDA) (Aldrich) and oxydiphthalic dianhydride (ODPA) (Aldrich) were dried in a vacuum oven at 150 ºC prior to use. 4,4'-Diaminodiphenyl Ether-2,2'-disulfonic Acid (ODADS), poly(sodium 4-styrenesulfonate) (PSS) and 1-butyl-3-methylimidazolium bis(trifluoromethane sulfone)imide (BMIm-NTFSI) were synthesized as previously reported.[9c, 23] 2,2'-Benzidinedisulfonic acid (BDSA) was washed with water and then dissolvent in water by adding TEA. Acidification with 1M H_2SO_4 (aq) precipitated pure BDSA. The TEA form of 4,4'-Diaminodiphenyl Ether-2,2'-disulfonic Acid (ODADS) and 2,2'-Benzidinesulfonic acid (BDSA) were dispersed in ethanol at 60 ºC then TEA was added to achieve complete dissolution. After cooling at 0 ºC overnight, the precipitate was filtered off, washed with ethanol, and dried under vacuum.

S1.2. Characterization

FT-IR spectra were obtained with a Nicolet Avatar 320 FTIR spectrometer; 32 scans were collected at a spectral resolution of 1 cm^{-1}. The XPS measurements were performed with ESCA 2000 systhem (VG Microtech) using a monochromatized aluminum Kα anode. Wide-angle X-ray diffraction (WAXD) 10 spectra were recorded for powdered samples using a Rigaku D/max-2500 type X-ray diffraction instrument. A DuPont Q100 thermo-gravimetric analyzer (TGA) was 25 utilized to investigate the thermal stability of the membranes; the samples (~10 mg) were heated from ambient temperature to 850 °C under a nitrogen atmosphere at a heating rate of 20 ºC min^{-1}. The molecular characteristics of poly(1-vinyl-3-butylimidazolium) bromide [PIL-(Br)] were determined by gel permeation chromatography (GPC, Waters Breeze). Tetrahydrofuran (THF) was used as an eluent, and the PS standard was used for calibration.

S1.3. Synthesis of Sulfonated Polyimide (SPI)

In a one-pot high temperature imidization process, control over the molecular weight and end group functionality was achieved using stoichiometrically adjusted amounts of the monomers (**Fig. S9**). A completely dried 150-mL four-neck flask was charged with PDDA (0.87 g, 2 mmol), BDSA (TEA form) (3.72 g, 8 mmol) and *m*-cresol (68 mL) with stirring under an Ar flow. After the BDSA (TEA form) had completely dissolved, PMDA (2.18 g, 10 mmol) and benzoic acid (1.75 g) were added. The reaction mixture was heated at 80 °C for 6 h and the mixture heated at 180 °C for another 24 h. The resulting polymer solution was precipitated into isopropanol (IPA). The polymer was filtered off, purified through Soxhlet extraction with methanol overnight, and then dried at 120 °C in vacuo for at least 24 h (yield: 90%). Sulfonated polyimide SPI (ODADS series) was synthesized and purified using the same procedure, and BDSA and PMDA were replaced by ODADS and ODPA, respectively (yield: 93%).



Scheme. S1. Schematic representation of the preparation of the SPI

Table S1. Characterization of SPI (PDDA-BDSA-PMDA) and SPI (PDDA-ODADS-ODPA)

Membrane	Ion exchange capacity (meq/g)		
	Calculated IEC_{th} [a]	Titrationi IEC_{tit} [b]	IEC_{tit}/IEC_{th} (%)
SPI (PDDA-BDSA-PMDA)	2.49	2.31	92.8
SPI (PDDA-ODADS-ODPA)	2.14	2.01	93.9

[a] IEC calculated from DS.

[b] IEC measured with titration.

S2. FT-IR spectrum of graphene oxide

There are four main peaks centered at 1052, 1402 and 1738 cm^{-1}. The peak at 1052 cm^{-1} arises from epoxy (-O-) groups. The peak at 1738 cm^{-1} corresponds to the vibrational mode of the ketone (-C=O) groups. The peak observed at 1402 cm^{-1} is assigned to a C-O vibrational mode.

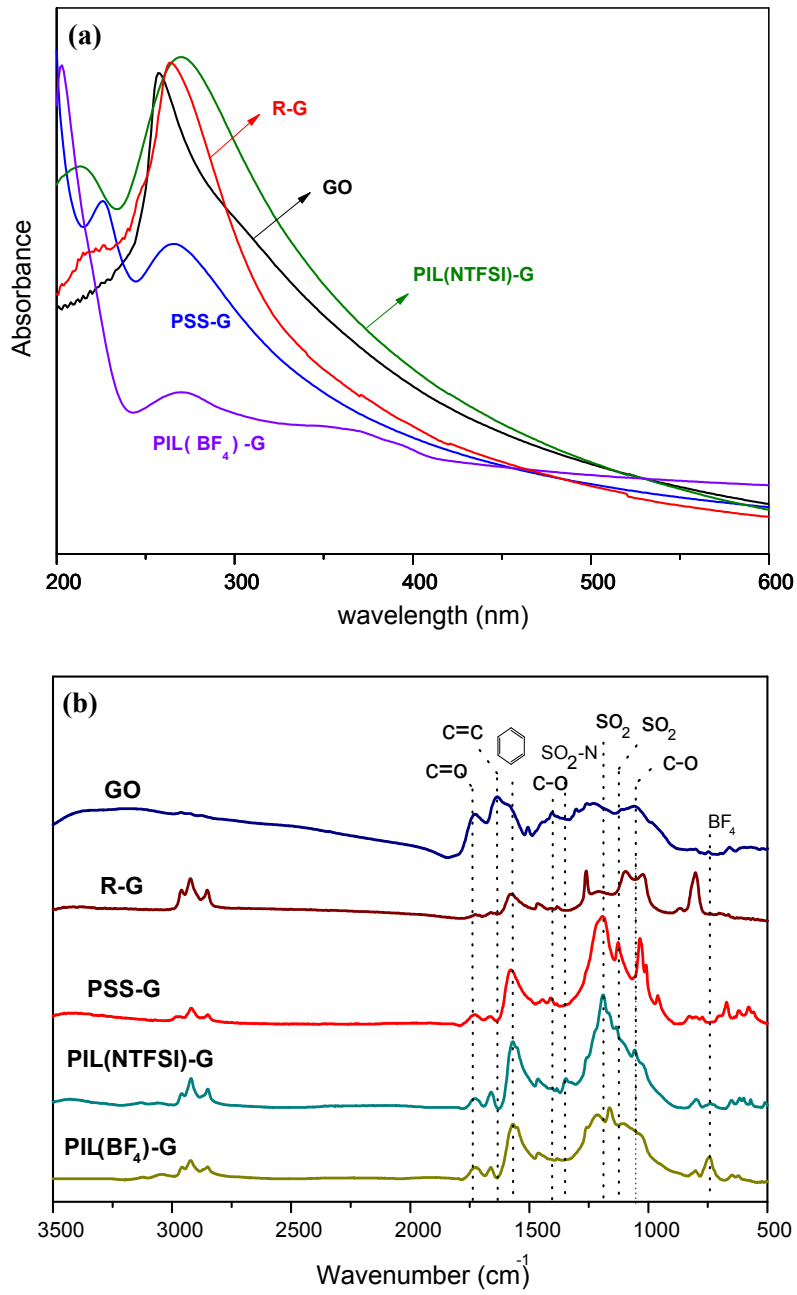


Fig. S1. (a) UV and (b) FT-IR spectra of GO, reduced GO (R-G), and an organic phase suspension of PSS-G, PIL(NTFSI)-G and PIL(BF_4)-G.

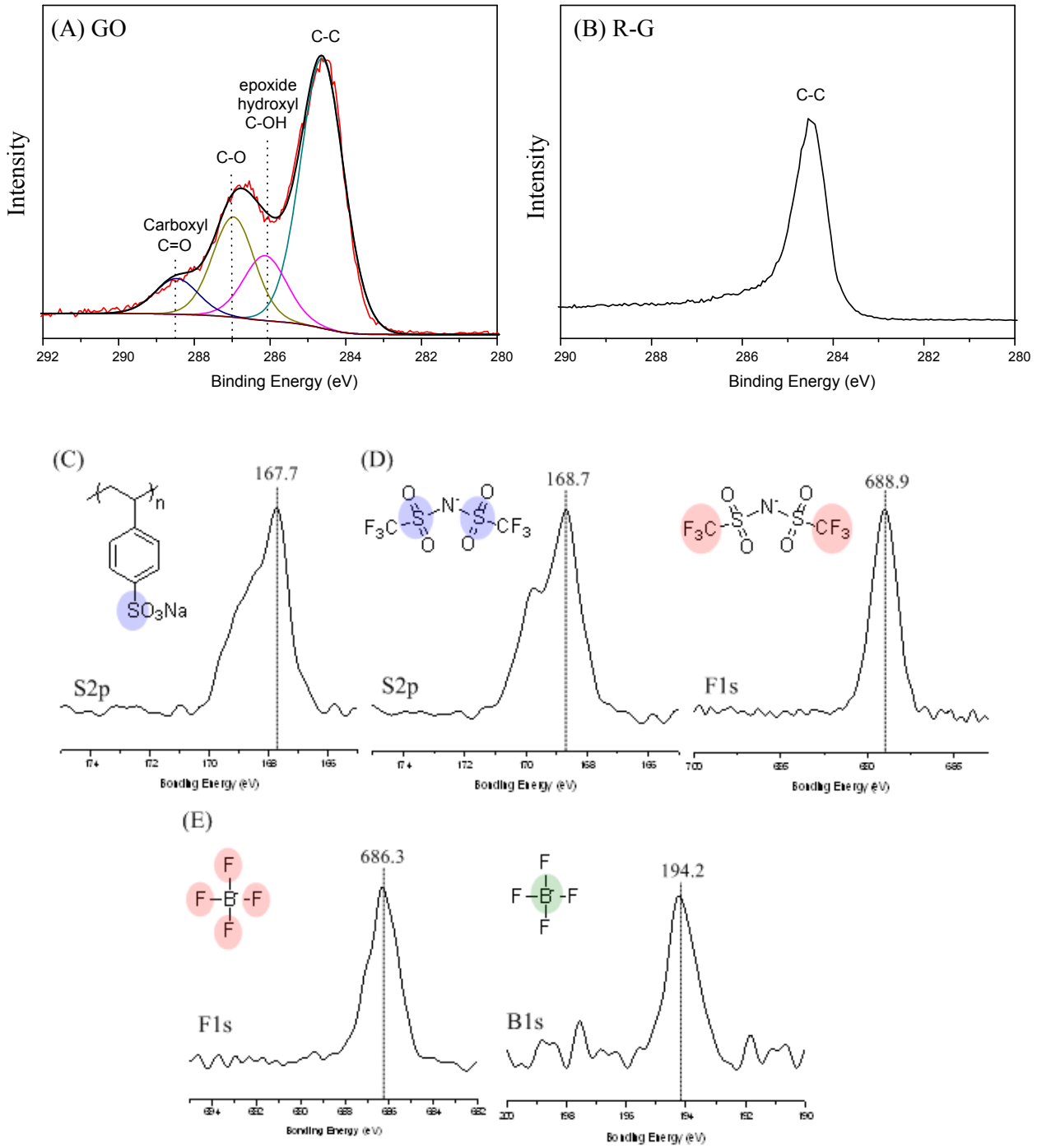


Fig. S2. (a) Carbon 1s XPS profile of GO and (b) R-G; comparison of XPS profile (c) PSS-G, (d) PIL(NTFSI)-G and (e) PIL(BF_4)-G.

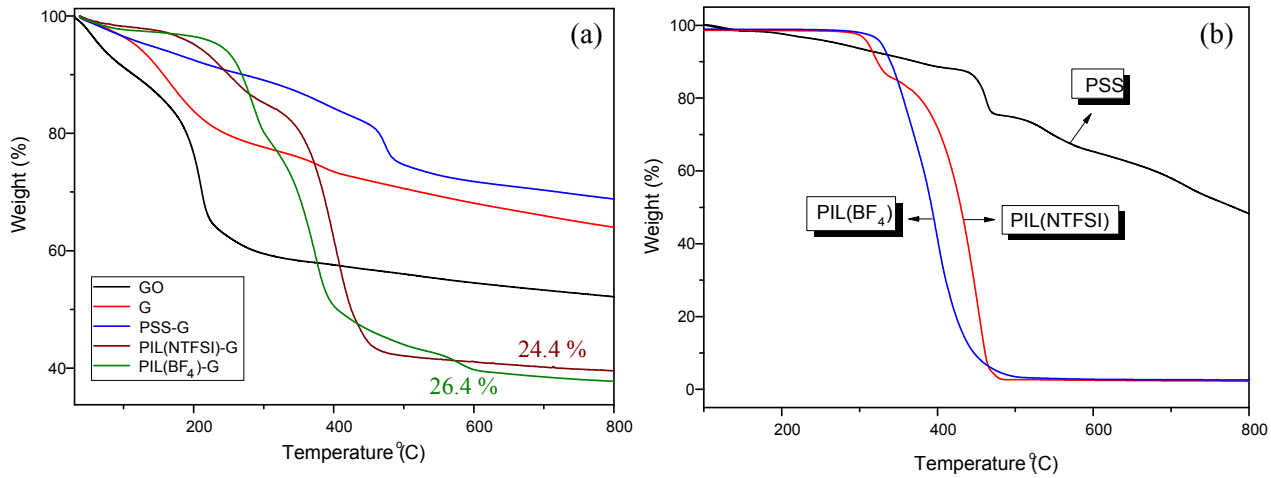


Fig. S3. TGA curves of (a) GO, R-G and modified graphene; (b) TGA curves of pure PSS, PIL(NTFSI) and PIL(BF_4).

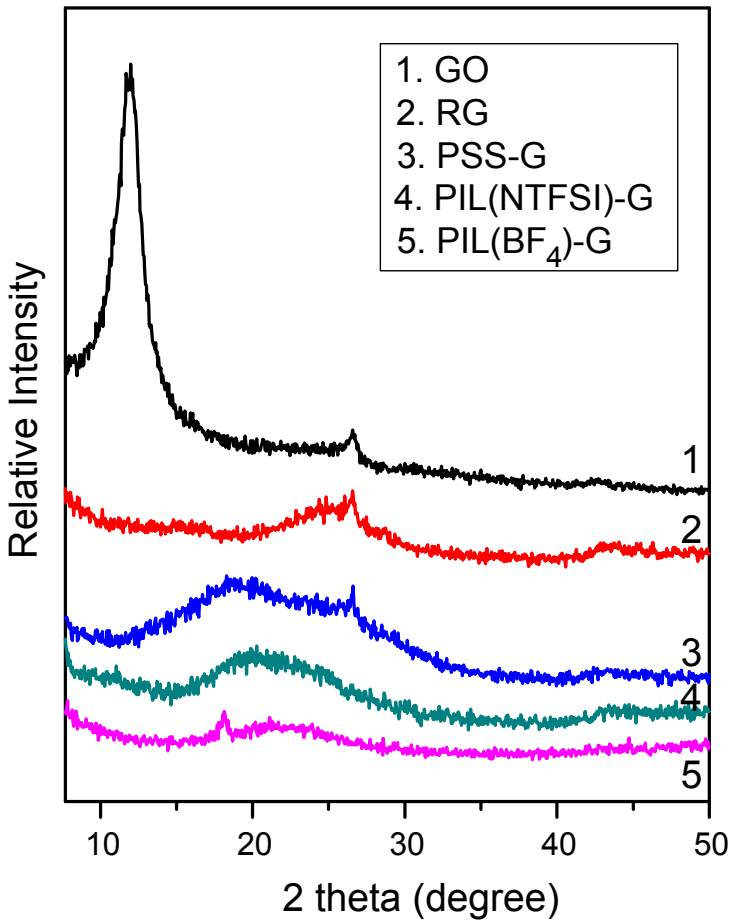


Fig. S4. XRD curves of the GO, R-G, PSS-G, PIL(NTFSI)-G and PIL(BF_4)-G.

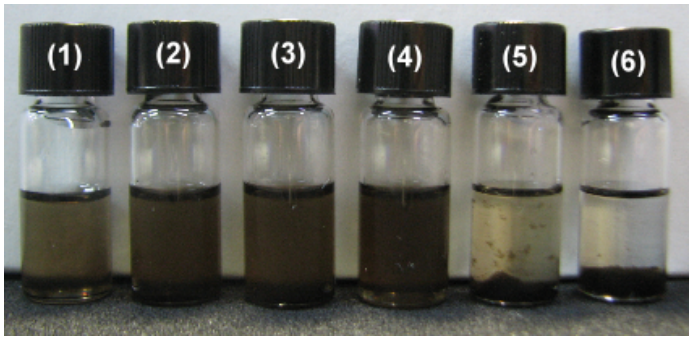


Fig. S5. Photographs of (1) - (3) correspond to DMSO dispersion of the GO (0.25 mg ml^{-1}) mixed with PIL-NTFSI, SPI and PSS and the weight ratio of the polymer to GO was 10; photographs of (4) - (6) correspond to (1) - (3) after being mixed with BMIm-NTFSI of 2.5 mg by shaking vigorously and then depositing for 30 min.

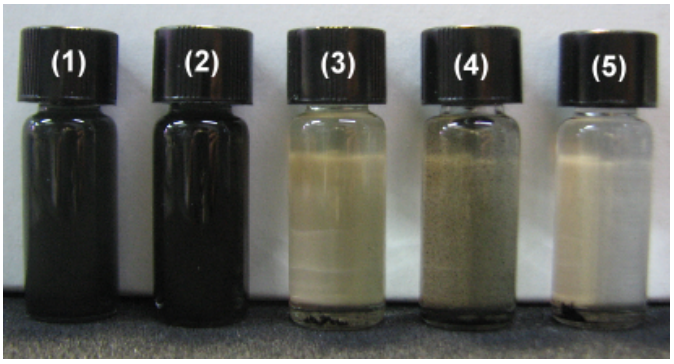


Fig. S6. Photographs of (1) - (5) correspond to BMIm-NTFSI dispersion of the (1) PIL(NTFSI)-G, (2) PIL(BF_4)-G, (3) PSS-G, (4) R-G and (5) GO (0.25 mg ml^{-1}).

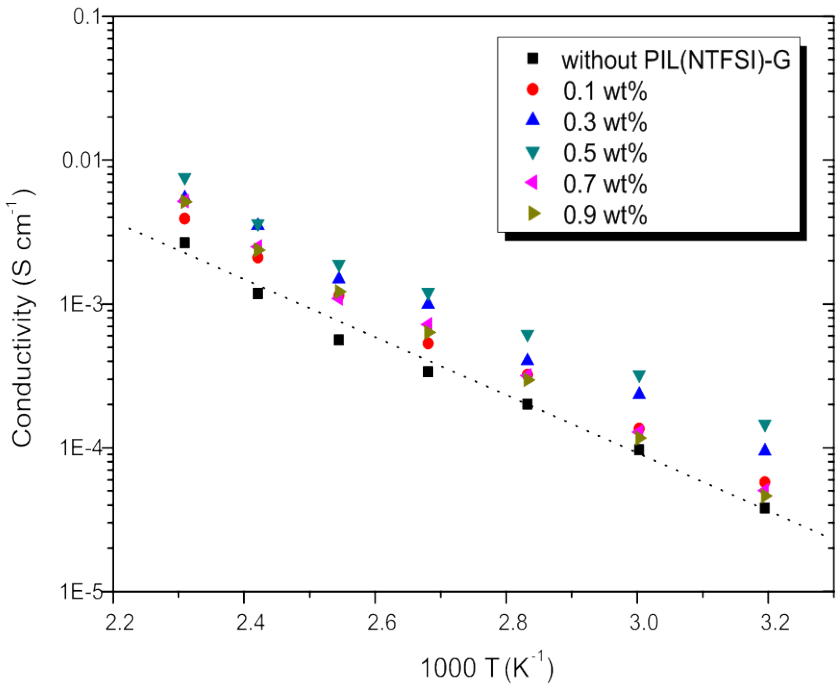


Fig. S7. Ionic conductivities as a function of temperature of SPI/PIL(NTFSI)-G/PIL membranes in anhydrous conditions.

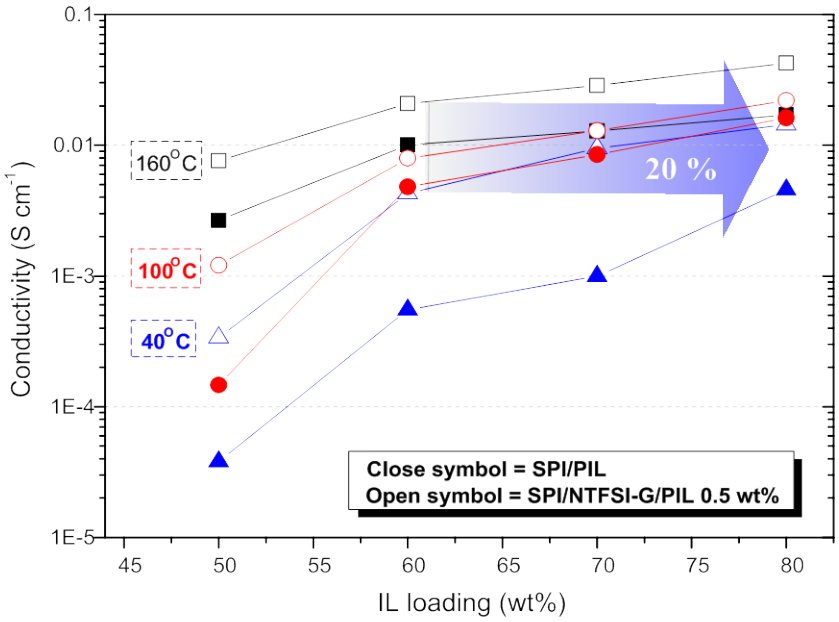


Fig. S8. The ionic conductivities of membranes incorporating the same amounts of PIL(NTFSI)-G (0.5 wt %) with various ratios of IL (50 ~ 80 wt%).

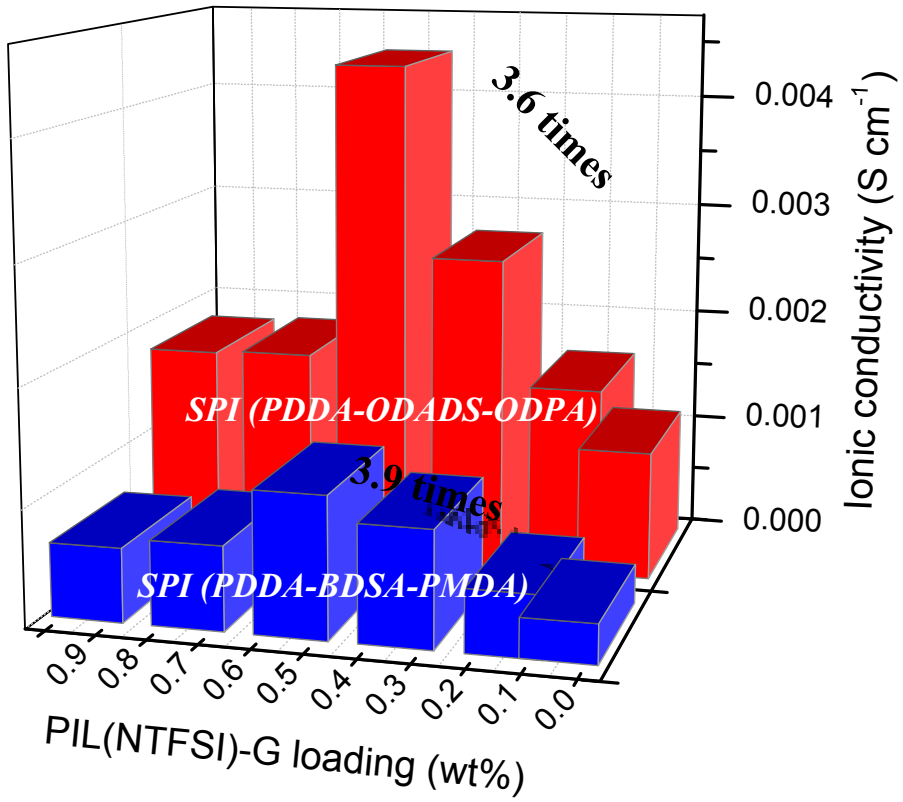


Fig. S9 The ionic conductivities of membranes incorporating the same amount of PIL(NTFSI)-G (0.5 wt %) with various ratios of PIL (50 ~ 80 wt%).

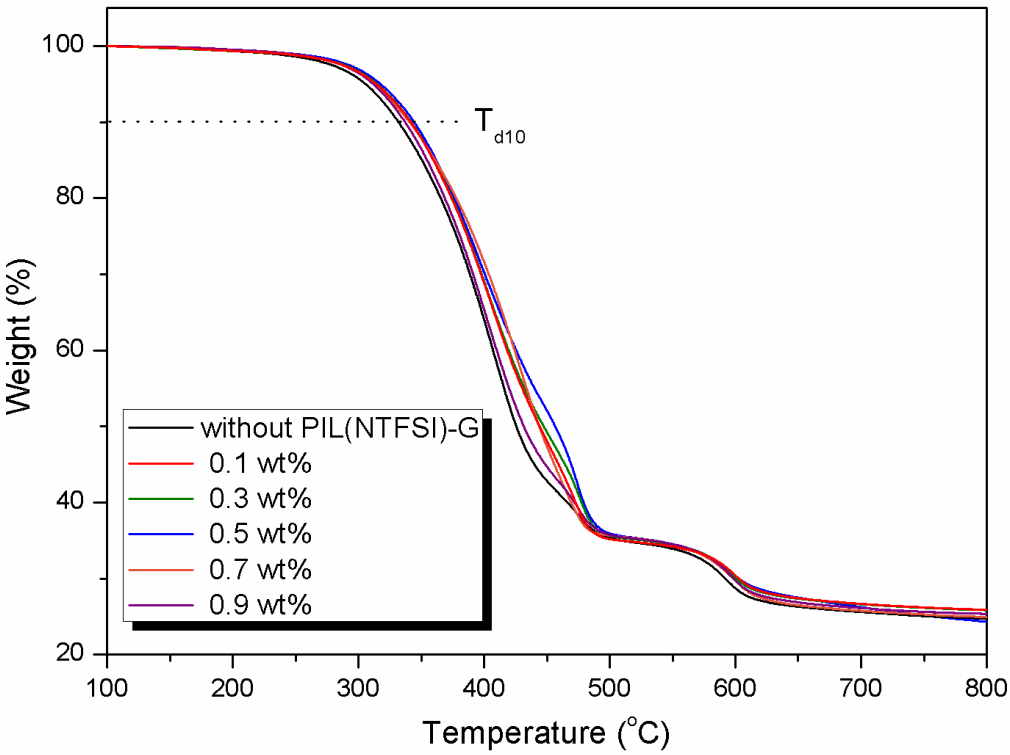


Fig. S10 TGA curves of SPI/PIL(NTFSI)-G/PIL composite membranes.

REFERENCES AND NOTES

1. (a) Ye, Y.-S.; Cheng, M.-Y.; Tseng, J.-Y.; Liang, G.-W.; Rick, J.; Huang, Y.-J.; Chang, F.-C.; Hwang, B.-J., New Proton Conducting Membranes with High Retention of Protic Ionic Liquids. *Journal of Materials Chemistry* **2011**; (b) Ye, Y.-S.; Chen, W.-Y.; Huang, Y.-J.; Cheng, M.-Y.; Yen, Y.-C.; Cheng, C.-C.; Chang, F.-C., Preparation and characterization of high-durability zwitterionic crosslinked proton exchange membranes. *Journal of Membrane Science* **2010,** *362* (1-2), 29-37; (c) Fang, J.; Guo, X.; Harada, S.; Watari, T.; Tanaka, K.; Kita, H.; Okamoto, K.-i., Novel Sulfonated Polyimides as Polyelectrolytes for Fuel Cell Application. 1. Synthesis, Proton Conductivity, and Water Stability of Polyimides from 4,4‘-Diaminodiphenyl Ether-2,2‘-disulfonic Acid. *Macromolecules* **2002,** *35* (24), 9022-9028.