Electronic Supplementary Material (ESI) for RSC Advances.

Toward improved mechanical strength, oxidative stability and proton conductivity of an aligned quadratic hybrid (SPEEK/FPAPB/Fe_3O_4-FGO) membrane for application in high temperature and low humidity fuel cells

Supporting information

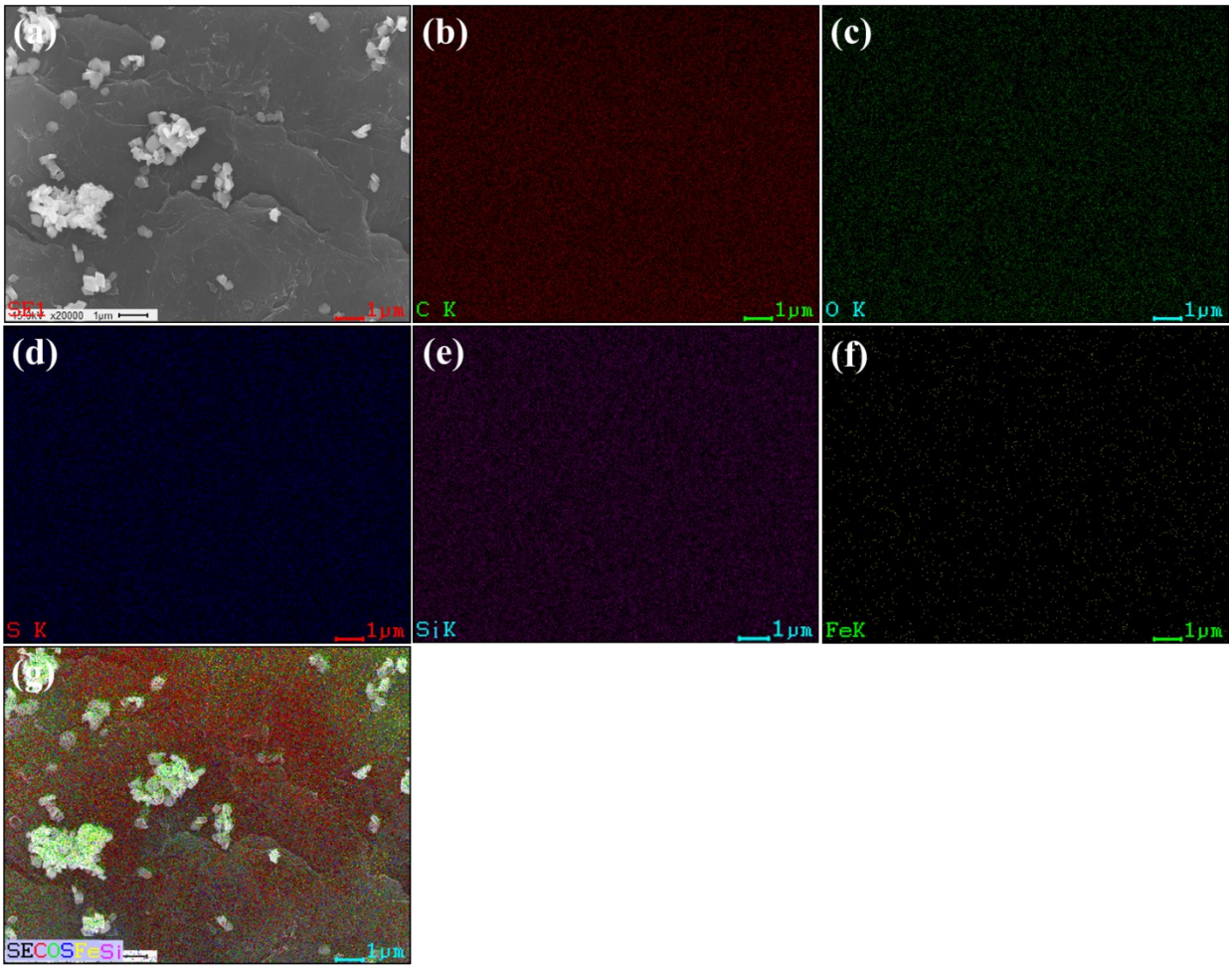

Fig. S1 (a) FE-SEM image of selected area of Fe_3O_4-FGO; corresponding EDX elemental mapping of (b) carbon, (c) oxygen, (d) sulfur, (e) silicon, (f) iron and (g) overlapping of elements.

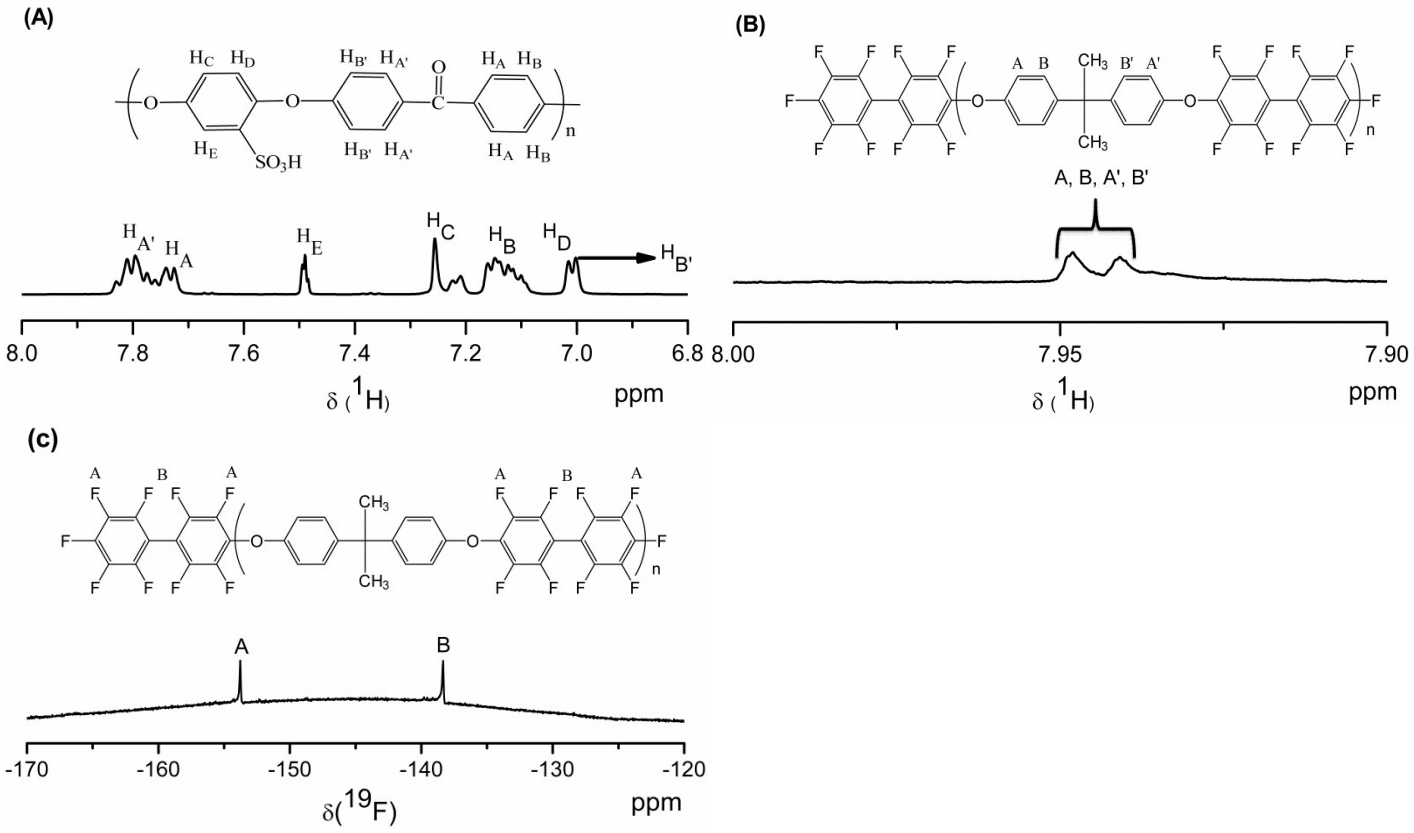

Fig. S2 ^{1}H-NMR spectra of (A) SPEEK and (B) FPAPB; ^{19}F-NMR spectrum of (C) FPAPB.

NMR

NMR was utilized to investigate the chemical structures of SPEEK and FPAPB, and the spectra are displayed in Fig. S2. Fig. S2A shows the ^{1}H–NMR spectrum of SPEEK in DMSO-d_6. In this spectrum, the signals appear at various frequencies range from 7.86 to 6.96 ppm and are assigned to H_A, $H_{A'}$, H_B, $H_{B'}$, H_C, H_D and H_E protons. The remaining satellite peaks found in the spectrum are attributed to the terminal protons in the polymer chain. The signal of the H_E proton (hydroquinone ring proton) is specifically affected by adjacent electron withdrawing sulfonic acid group while compared to other protons. The DS of the SPEEK, which is 65%, was evaluated from ratio of the peak area of H_E proton and sum of the peak areas of other protons using the equation given below:

$$\frac{n}{12-2n} = \frac{AH_E}{\sum AH_{A,A',B,B',C,D}}$$

where n is the number of H_E protons per unit and A is the peak area.

Fig. S2B shows the ^{1}H–NMR spectrum of FPAPB in DMSO-d_6. The signals at frequency range between 7.95 and 7.93 ppm are attributed to the A, A', B and B' protons nearer to the decafluorobiphenyl rings. Fig. S2C exhibits the ^{19}F–NMR spectrum of FPAPB in DMSO-d_6. The high field signal observed at the frequency range of –153 ppm is related to the A fluorine atoms, whereas the low field signal observed between the frequency range of –138 ppm is attributed to the B fluorine atoms in the FPAPB.

GPC

To reach desired viscosity and density for the FPAPB polymer solution, the GPC experiment was conducted in DMF solvent at 60℃. The LiBr (1g L^{-1}) was added into the solution to suppress the effect of polystyrene. The FPAPB polymer exhibited a number average molecular weight (M_n), weight average molecular weight (M_W) and mean average molecular weight (M_Z) of 8000, 31,000 and 80,500, respectively. Nevertheless, the calculated poly disperse index (PDI) of the polymer is 3.8. These results show that the synthesized FPAPB is effectively formed by an ideal nucleophilic substitution and polymerization reaction.

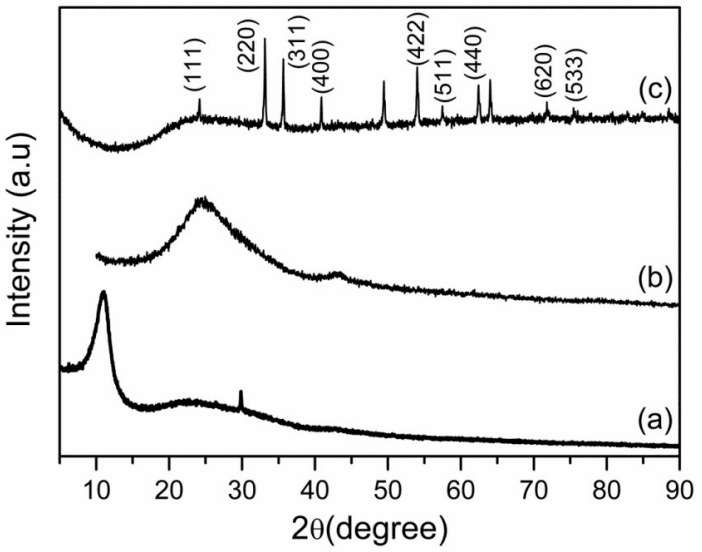

Fig. S3 XRD patterns of (a) GO, (b) FGO and (c) Fe_3O_4-FGO.

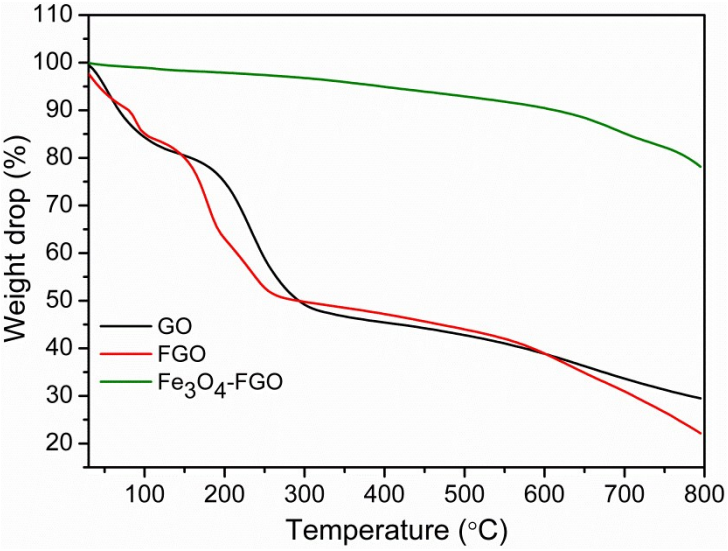

Fig. S4 TGA curves of GO, FGO and Fe_3O_4-FGO.

Properties	Temperature (˚C)	Membrane specimens		
		Pristine SP	SPFG-5	SPFSGF-5(unaligned)
Water uptake (%)	20	21.85	19.40	25.53
	40	34.63	31.18	37.90
	60	44.53	42.30	48.98
	80	soluble	54.61	59.13
Volume change (%)	20	15.45	8.61	13.80
	40	26.90	13.31	19.71
	60	35.13	22.51	27.30
	80	–	32.31	38.20
λ (H_2O/SO_3H)	20	7.58	6.94	8.53
	40	12.01	11.16	12.66
	60	15.45	15.14	16.37
	80	–	19.55	19.76

Table S1 Water uptake, volume change and hydration number of the pristine SP, SPFG-5 and SPFSGF-5 (unaligned) membranes.

Relative humidity (%)	Temperature (˚C)	Proton conductivity (mS/cm)		
		Pristine SP	SPFG-5	SPFSGF-5(unaligned)
100	20	20.61	11.33	24.79
	40	40.81	27.88	42.70
	60	47.59	40.20	50.49
	80	soluble	48.73	61.08
	100	soluble	59.96	72.75
20	20	2.18	2.69	3.76
	40	2.89	3.41	5.07
	60	3.95	4.75	6.13
	80	4.42	5.34	7.83
	100	6.01	6.81	8.32
	120	7.68	7.33	10.06

Table S2 Proton conductivities of pristine SP, SPFG-5 and SPFSGF-5 (unaligned) membranes under 100 and 20 % RH.

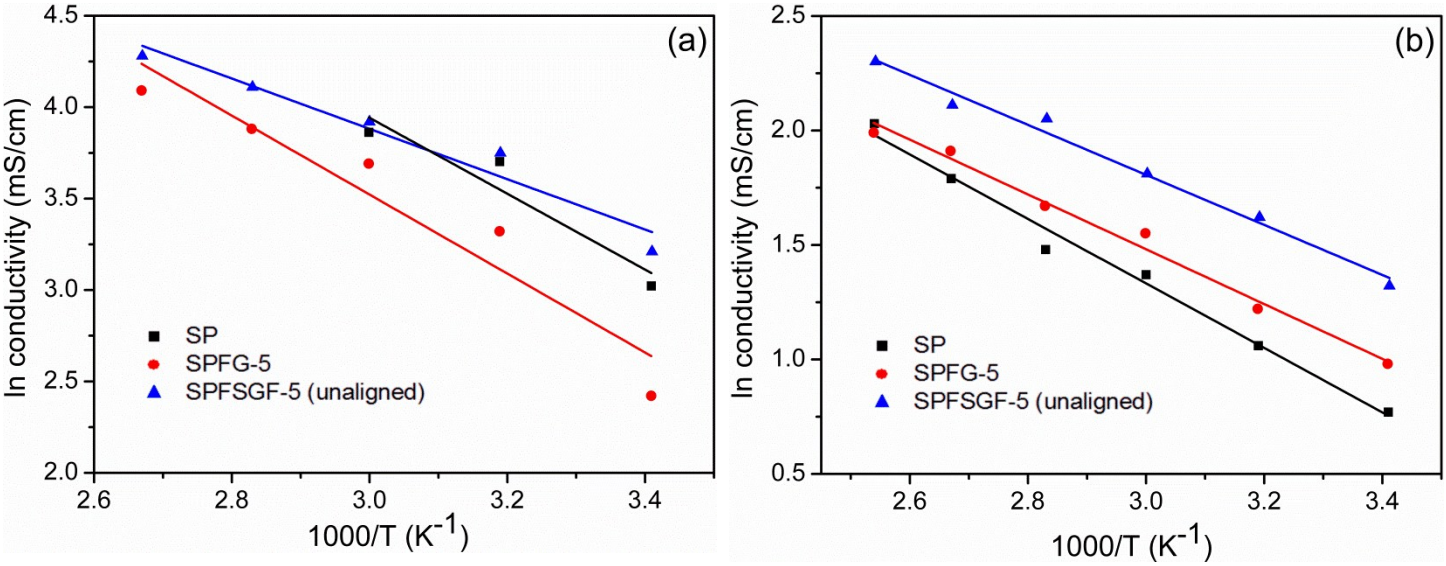

Fig. S5 Arrhenius plots for proton conductivities of pristine SP, SPFG-5 and SPFSGF-5 (unaligned) membranes (a) under 100% RH and (b) under 20% RH.

Membrane	IEC (meq/g)	Water uptake (%)	Water uptake temperature (°C)	Peak proton conductivity (mS/cm)	Operating conditions		Reference
					Relative humidity (%)	Temperature (°C)	
SPFSGF-5 (aligned)	1.66	62.15	80	75.16	100	100	This work
SPFSGF-5 (unaligned)	1.66	59.13	80	72.75	100	100	This work
Nafion/S-grapgene-1	0.96	27.3	25	17.0	20	90	6
SPEEK/S-GO-5	1.65	20.1	25	8.4	100	80	15
Nafion/F-GO	0.96	29.20	room temperature	47.0	30	120	21
PA-QSPEEK/FGO-3	–	–	–	35.7	Anhydrous	140	22
SPEEK/SSGO-5	1.66	30.1	25	3.56	Anhydrous	120	40
SPEEK/SDBS-GO-8	1.83	53.2	65	162.6	100	65	50
Nafion/S-GO-0.5	–	24.2	30	36.2	40	80	51
PVA/GLA/S-GO-5	0.92	58.3	room temperature	50	50	30	52
SPI/SPSGO-8	2.05	55.8	room temperature	96.2	100	30	53
SPAES/ABPBI-GO-1	–	22.8	room temperature	5.4	50	80	54
M_{SPSF5}	1.32	58.3	30	139	100	80	55
Chitosan/S4GO-2	0.31	59.7	25	11.0	Anhydrous	120	56
Nafion/SPEEK/SGO	–	71.2	90	322.2	100	90	57

Table