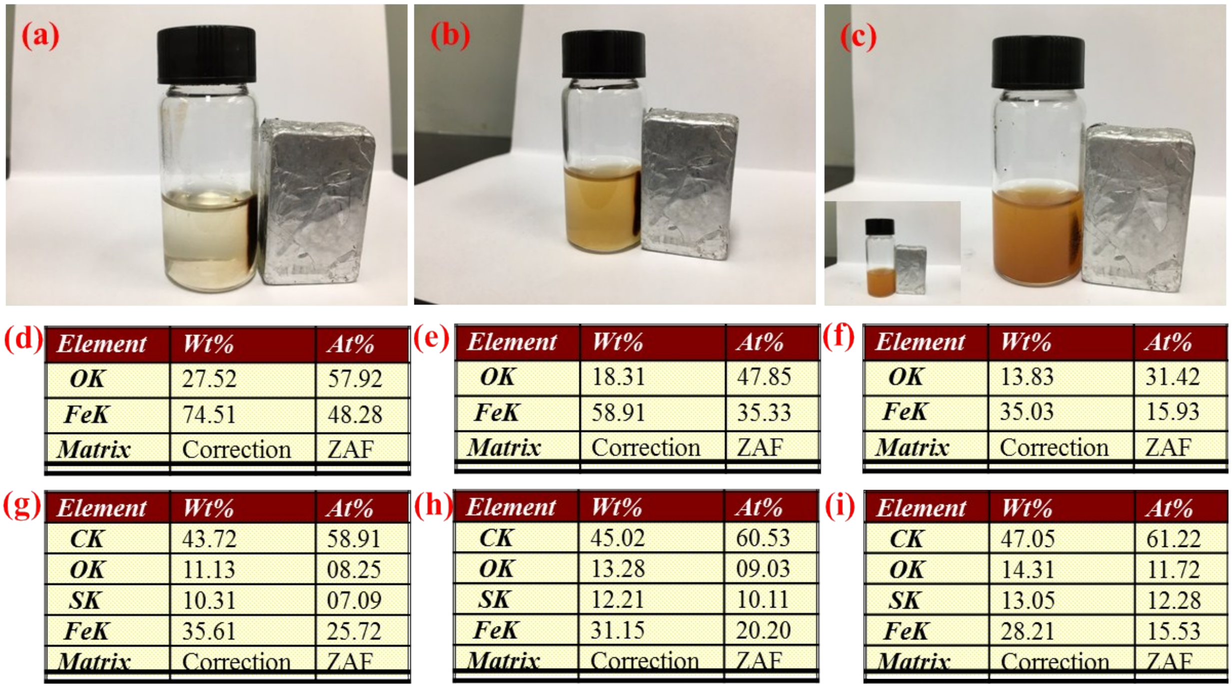
Sulfonated graphene oxide/Nafion composite membranes for high temperature and low humidity proton exchange membrane fuel cells

Supporting information



(d)

Element	*Wt%*	*At%*
OK	27.52	57.92
FeK	74.51	48.28
Matrix	Correction	ZAF

(e)

Element	*Wt%*	*At%*
OK	18.31	47.85
FeK	58.91	35.33
Matrix	Correction	ZAF

(f)

Element	*Wt%*	*At%*
OK	13.83	31.42
FeK	35.03	15.93
Matrix	Correction	ZAF

(g)

Element	*Wt%*	*At%*
CK	43.72	58.91
OK	11.13	08.25
SK	10.31	07.09
FeK	35.61	25.72
Matrix	Correction	ZAF

(h)

Element	*Wt%*	*At%*
CK	45.02	60.53
OK	13.28	09.03
SK	12.21	10.11
FeK	31.15	20.20
Matrix	Correction	ZAF

(i)

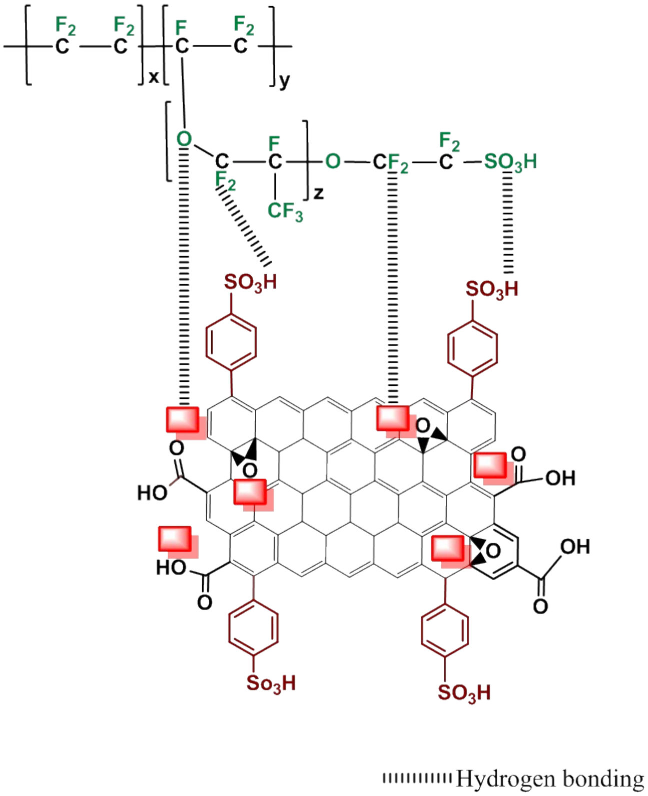
Element	*Wt%*	*At%*
CK	47.05	61.22
OK	14.31	11.72
SK	13.05	12.28
FeK	28.21	15.53
Matrix	Correction	ZAF

Fig. S1 Optical photographs of dissolution of Fe_3O_4 nanoparticles in 1 M H_2SO_4 at 70 °C at (a) 0 mins, (b) 30 mins, (c) 60 mins and inset (c) 90 mins; corresponding EDX spectra of remaining Fe_3O_4 nanoparticles at (d) 0 mins, (e) 30 mins and (f) 60 mins; EDX spectra of remaining Fe_3O_4-SGO composite after immersed in 1 M H_2SO_4 at 70 °C at (g) 0 mins, (h) 30 mins and (i) 60 mins.

Hydrolytic stability of GO, SGO and Fe_3O_4-SGO

In general, the performance of PEFC is strictly affected by metal/metal oxide leaching out from the composite PEM in an acidic environment. In present study, the hydrolytic stability of Fe_3O_4 and Fe_3O_4-SGO composite was measured in 1 M acidic solution (pH<1) at 70 °C to understand the dissolution of Fe_3O_4, as shown in Fig. S1. An amount of Fe_3O_4 or Fe_3O_4-SGO was added in 1 M H_2SO_4 (5 mg mL^{-1}) and the mixture was stirred at 70 °C for desired time. After dissolution, the remaining Fe_3O_4 nanoparticles were separated by magnetic bar, while Fe_3O_4-SGO was separated by filtration due to its trivial magnetic behavior. The stability of fillers was assessed from wt% of Fe in remaining sample at 30 mins intervals. The EDX spectra were collected at three different regions in each sample and displayed value is the average of data. It can be seen that Fe_3O_4 dissolves completely at 90 mins of time and rapid dissolution of

Fe_3O_4 may be due to the formation of corresponding hydroxides (Fig. S1c inset). After 60 mins of time, the wt% of Fe in Fe_3O_4 and SGO-Fe_3O_4 were found to decrease from 74.51 to 35.03 and from 35.61 to 28.21, respectively. These results indicate that the leaching of Fe_3O_4 is very less after anchoring over SGO surface. It is noteworthy to mention that Fe_3O_4 nanoparticles are surrounded by SGO sheets and held tightly in the matrix. Such geometric confinement enhances the interactions at the interface of Fe_3O_4 and SGO, thereby reducing the dissolution and aggregation of Fe_3O_4 nanoparticles in acidic environment. Furthermore, the extended sheets of SGO perform as barrier to prevent the direct contact of acid and Fe_3O_4 nanoparticles, which further reduces the dissolution of Fe_3O_4 nanoparticles in composite.



Scheme S1 Possible interactions exerted between Nafion and Fe_3O_4-SGO.

Table S1 Comparison of various Nafion composite membranes.

Membrane	**Proton conductivity (mS cm^{-1})**	**Operating conditions**		**Peak power density (mW cm^{-2})**	**Peak current density (mA cm^{-2})**	**Operating conditions**		**Reference**
		Temperature (˚C)	**Relative humidity (%)**			**Temperature (˚C)**	**Relative humidity (%)**	
Nafion/FGO	18.21	120	20	150	600	120	25	1
Nafion/TNT	8.2	80	20	650	2270	80	18	4
Nafion–S-graphene	17	80	20	300	1095	70	20	17
Nafion/GO	120	90	40	–	–	–	–	56
Nafion/GO-poly(SPM-*co*-PEGMEMA)	29.8	80	40	132	588	60	50	57
Nafion/SPEEK/HGO	322.2	90	100	621.2	1596	80	100	58
Nafion/GO	44	120	–	212	788	100	25	59
Nafion/GO	90	80	100	600	1700	70	40	60
Nafion/sMC	79	80	40	660	1800	70	20	61
Nafion/ZrNT	6	80	20	572	2000	80	18	62
Nafion/TiO_2	121	90	50	–	1600	90	50	63
Nafion/PTA	13	120	35	–	750	120	35	64
Nafion/PW-mGO	10.4	80	25	841	2700	80	20	65
Nafion/TNT-10	9	80	20	641	2240	80	18	66
Nafion/Fe_3O_4-SGO	11.62	120	20	258.82	830.51	120	25	This work