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Supporting Information

Efficient and durable composite membranes based on polydopamine-mediated sulfonated graphene oxide for direct methanol fuel cells

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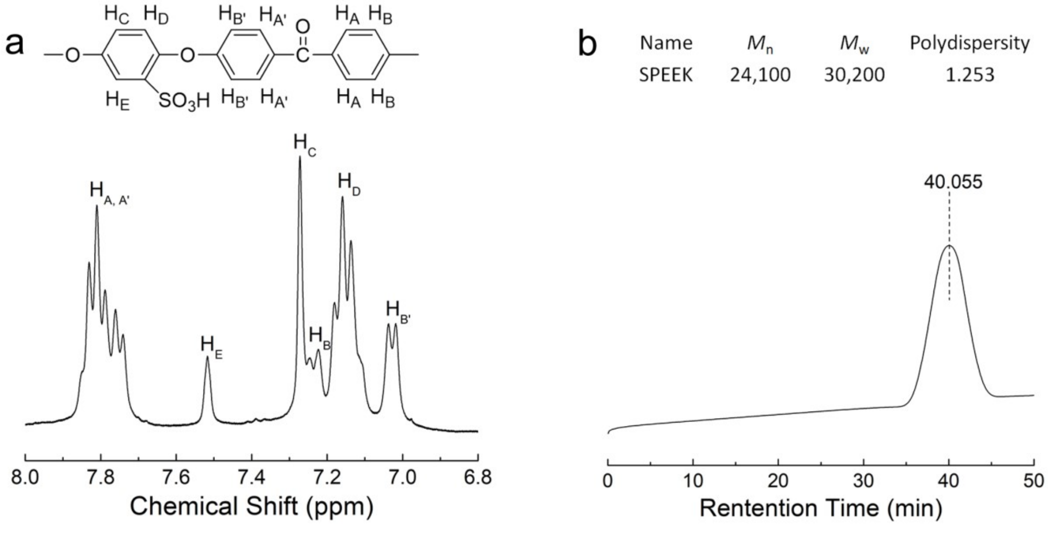
Supplementary Note 1 Degree of sulfonation (DS) and weight-average molecular weight (M_w) of SPEEK

The DS of SPEEK was determined by ^{1}H nuclear magnetic resonance (NMR) spectrum on an Avance III HD NanoBAY spectrometer (Bruker, Germany), before which polymer was dissolved in deuterated dimethyl sulfoxide as ~ 3 wt% solution. In Fig. S1a, the signal at ~ 7.5 ppm represents protons located at the ortho position of sulfonic acid groups (H_E). The signal intensity or peak area of H_E and all the other proton signals could be used to determine the DS of SPEEK as follows:

$$\frac{\mathrm{DS}}{12-2\mathrm{DS}} = \frac{A_{\mathrm{H_E}}}{\sum A_{\mathrm{H_{A,A',B,B',C,D}}}}$$

where $A_{\mathrm{H_E}}$ and $A_{\mathrm{H_{A,A',B,B',C,D}}}$ represent the integrated peak area of H_E and all the other aromatic hydrogens, respectively. The DS of SPEEK is determined to be 49.0%.

The weight-average molecular weight of the SPEEK was determined by gel permeation chromatography on an Agilent 390LC MDS instrument (Agilent, USA) using dimethylformamide containing 6 mmol ammonium tetrafluoroborate as eluent at a flow rate of 1 mL min^{-1}. In Fig. S1b, the weight-average molecular weight of the SPEEK is determined to be ~ 30200 according to the retention time of 40.055 min.



Name	M_n	M_w	Polydispersity
SPEEK	24,100	30,200	1.253

Fig. S1. (a) ^{1}H NMR spectrum and (b) GPC retention time of SPEEK

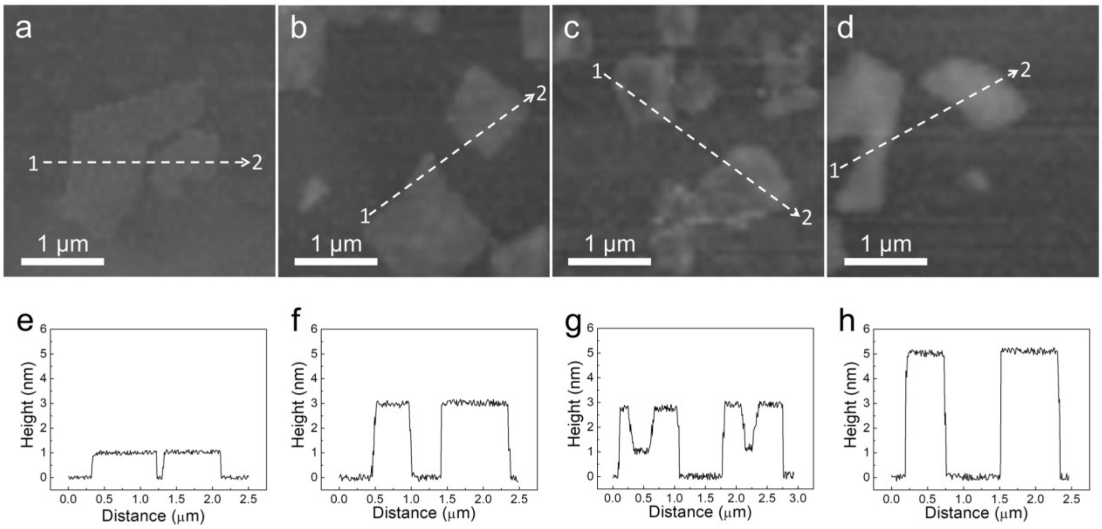


Fig. S2 AFM morphology of (a) pristine GO, (b) DGO, (c) SGO and (d) SDGO, and sheet thickness measurement of (e) pristine GO, (f) DGO, (g) SGO and (h) SDGO. The height curves in (e-f) correspond to the scans along the dashed lines (from point 1 to point 2) in (a-d), respectively. Pristine GO (a and e) has a uniform surface morphology with a sheet thickness of ~ 1.0 nm. By PDA coating, the thickness of DGO (b and f) evenly grows to ~ 3.0 nm, indicating the PDA coating of ~ 1.0 nm thickness on the surface of both sides on pristine GO. Direct ATRP process on GO leads to inhomogeneous surface of SGO (c and g). Some areas reach a thickness of 2.8 nm, but other parts almost maintain the thickness similar to pristine GO (~ 1.0 nm), due to the uneven distribution of hydroxyl groups for the ATRP initiation. In comparison, SDGO (d and h) display very uniform surface with a thickness of ~ 5.0 nm. These results further demonstrate the much improved functionalization uniformity/sufficiency of SDGO over SGO.

Table S1 τ_3 and I_3 obtained from PALS and free volume radius r calculated from τ_3

Membrane	τ_3 (ns)	I_3 (%)	r (nm)
SPEEK	1.81	1.12	0.267
SPEEK-4GO	2.01	13.26	0.286
SPEEK-4DGO	1.87	8.41	0.273
SPEEK-4SGO	1.97	6.13	0.282
SPEEK-4SDGO	1.83	1.64	0.269

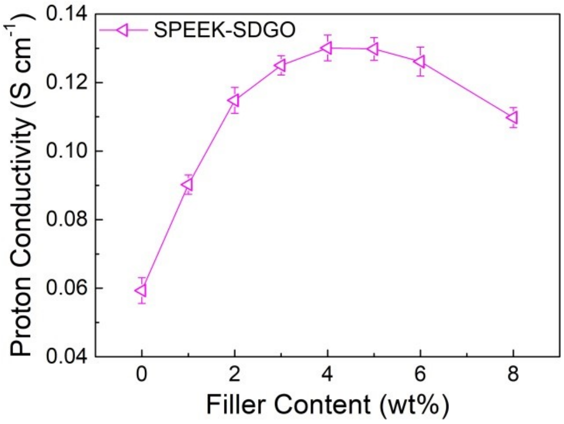


Fig. S3. Proton conductivity of SPEEK-SDGO composite membranes with different SDGO loadings (0-8 wt%) at 60 °C in water

Supplementary Note 2 Further discussion on selecting the DGO (10 h PDA deposition) and SDGO (18 h ATRP process) used for membrane preparation.

Generally, the amount of deposited PDA could affect the subsequent ATRP process as well as membrane durability, and the ATRP process will have evident influence on membrane performance, such as proton conductivity. Since we focus on pursuing both high-performance and durability of the SPEEK-SDGO composite membranes, a comprehensively balanced experimental route should be selected so that overall membrane quality is optimized. Detailed rationales for selecting the DGO (10 h PDA deposition) and SDGO (18 h ATRP process) used for membrane preparation are discussed below alongside Fig. S4, S5 and S6.

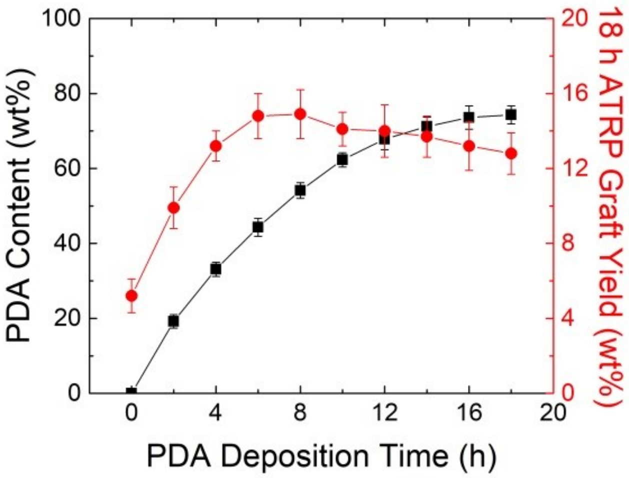


Fig. S4 Relationship between PDA deposition time and PDA content on DGO (left y-axis, black); and relationship between 18 h ATRP graft yield of PSSA and PDA deposition time of DGO (right y-axis, red).

As shown in Fig. S4, at a uniform ATRP time (18 h), DGOs with the initial increase of PDA deposition time (0-6 h) display fast growing graft yield of PSSA, as the deposited PDA coating provides more hydroxyl initiation sites. The highest ATRP graft yield is achieved by the DGO with 6-8 h PDA deposition time. With further increase of PDA deposition time (> 8 h), slight decline is observed for ATRP graft yield onto DGO. This is because after the whole surface of GO is coated by PDA, further deposition of PDA mainly increase the volume/weight of DGO, but the surface area (i.e., the amount of available hydroxyl initiation sites on the surface) remains almost unchanged, which decreases the specific surface area of DGO for ATRP reaction and leads to the lower ATRP graft yield.

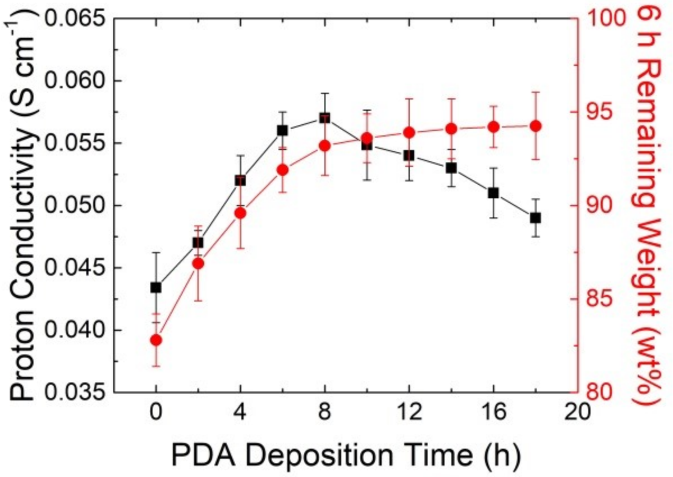


Fig. S5 Relationship between PDA deposition time and proton conductivity of SPEEK-DGO (4 wt%) composite membrane (left y axis, black), or the remaining weight of SPEEK-DGO (4 wt%) composite membrane after the immersion in Fenton's reagent (5 ppm Fe^{2+}/3% H_2O_2) for 6 h (right y axis, red).

The proton conductivity of SPEEK-DGO (4 wt%) composite membrane as the function of PDA deposition time shows a non-monotonic behavior (Fig. S5), with a peak value at around 6-8 h PDA deposition. This is in line with the effect to the ATRP graft yield (right y axis of Fig. S4), as the proton channels facilitated along DGO in the composite membrane also mainly derives from the matrix-filler interface (i.e. specific surface area of the incorporated 4 wt% DGO). As for the results of Fenton's test, the remaining weight of SPEEK-DGO (4 wt%) membrane exhibits obvious increase when PDA deposition time changes from 0 to 8 h, indicating considerable improvement of membrane durability due to the increased PDA content. When PDA deposition time further increases (> 8 h), the remaining weight of SPEEK-DGO (4 wt%) membrane levels off, suggesting the promotion of membrane durability by the PDA coating reaches the plateau. Such phenomenon could be also related to the reduced specific surface area of DGO after 8 h deposition. Based on the results in Fig. S4 and S5, 8 h appears to be the preferred PDA deposition time for DGO preparation. However, since the target membrane of this work is SPEEK-SDGO but not SPEEK-DGO, and the ATRP process will consume certain amount of PDA, we selected the DGO with a slightly longer PDA deposition time (10 h) for further functionalization, to optimize the performance and durability of SPEEK-SDGO membranes.

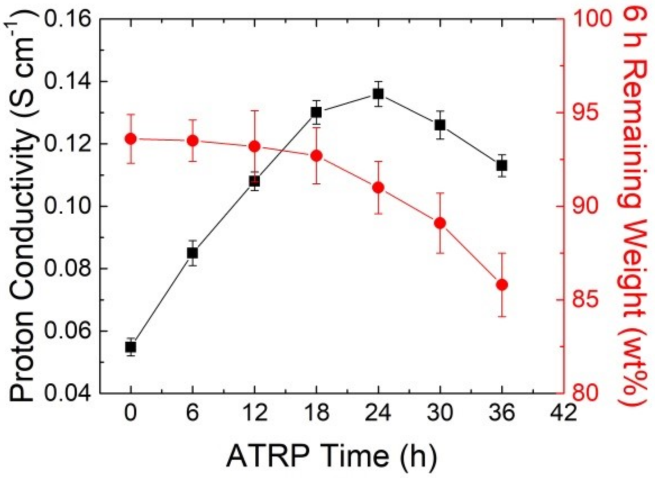


Fig. S6 Relationship between ATRP time (based on the DGO with 10 h PDA deposition) and proton conductivity of SPEEK-SDGO (4 wt%) composite membrane (left y axis, black), or the remaining weight of SPEEK-4SDGO (4 wt%) composite membrane after the immersion in Fenton's reagent (5 ppm Fe^{2+}/3% H_2O_2) for 6 h (right y axis, red).

As shown in Fig. S6, membrane proton conductivity reaches a maximum value at ATRP time of 24 h, where the initial growth (0-24 h) is attributed to the well facilitated proton-conducting channels along SDGO surface with the uniform and increased sulfonation, and the subsequent decline (> 24 h) could be correlated to the reduced specific surface area of SDGO. Since longer ATRP time leads to the decreased PDA content, the remaining weight of SPEEK-4SDGO (4 wt%) composite membrane after Fenton's tests shows a decreasing trend, and the decrease at ATRP time > 12 h appears to be accelerated, perhaps because of the degraded radical scavenging ability with the insufficient PDA content. Consequently, SDGO with 18 h ATRP time is selected to balance the overall optimized membrane performance and durability.

Table S2 IEC and E_a for proton transfer of SPEEK control and composite membranes

Membrane	IEC (mmol g^{-1})	E_a (kJ mol^{-1})
SPEEK	1.49±0.02	14.93
SPEEK-4GO	1.43±0.01	13.43
SPEEK-4DGO	1.40±0.02	12.34
SPEEK-4SGO	1.46±0.03	12.19
SPEEK-4SDGO	1.45±0.02	9.56

Table S3 Comparison with related studies on SGO composite membranes for DMFC

Ref.	Membrane formula	Membrane conductivity	Power density of DMFC	*In situ* durability of DMFC
1	SPEEK/ 5 wt% SGO	0.155 S cm^{-1} at 65 ^{o}C/in water	~ 65 mW cm^{-2} at 65 ^{o}C with 1 M methanol/O_2	Not reported
2	SPEEK/ 5 wt% SGO	0.136 S cm^{-1} at 65 ^{o}C/in water	~ 120 mW cm^{-2} at 80 ^{o}C with 1 M methanol/O_2	11.4% voltage loss after 60 h constant current density test at 65 ^{o}C with 1 M methanol/O_2
3	SPEEK/ 2.5 wt% SGO	0.0945 S cm^{-1} at 30 ^{o}C/in water	Not reported	Not reported
4	SPEEK/ 0.15 wt% SGO	0.0738 S cm^{-1} at 80 ^{o}C/in water	170 mW cm^{-2} at 80 ^{o}C with 2 M methanol/O_2	Evident current density loss after 100 h OCV holding at 80 ^{o}C with 2 M methanol/dry O_2
5	Nafion/	~ 0.123 S cm^{-1}	132 mW cm^{-2} at 60 ^{o}C	Not reported

	0.5 wt% SGO	at 100 ^{o}C/in water	with 1 M methanol/O_2	
6	Nafion/ 0.8 wt% SGO	0.0481 S cm^{-1} at 50 ^{o}C/40% RH	Not reported	Not reported
7	PBI/ 25 wt% SGO	0.0412 S cm^{-1} at 90 ^{o}C/100% RH	Not reported	Not reported
8	SPI/ 8 wt% SGO	0.0962 S cm^{-1} at 30 ^{o}C/in water	75.06 mW cm^{-2} at 70 ^{o}C with 2 M methanol/air	~ 13% current density loss after 70 h constant voltage test at 100 ^{o}C with 2 M methanol/air
9	Free standing stacked SGO	0.0918 S cm^{-1} at 65 ^{o}C/in water	~ 40 mW cm^{-2} at 80 ^{o}C with 1 M methanol/air	~ 7% voltage loss after 23 h constant current density test at 65 ^{o}C with 1 M methanol/air
This work	SPEEK/ 4 wt% PDA-mediated SGO	0.162 S cm^{-1} at 80 ^{o}C/in water	177.93 mW cm^{-2} at 80 ^{o}C with 1 M methanol/O_2	(1) 4.4% OCV loss after 240 h chemical AST (OCV holding) at 80 ^{o}C with 5 M methanol/dry O_2; (2) 3.7% OCV loss after 240 h mechanical AST (1440 RH cycles) at 80 ^{o}C; (3) 2.5% current density loss after 480 h constant voltage test at 60 ^{o}C with 1 M methanol/O_2

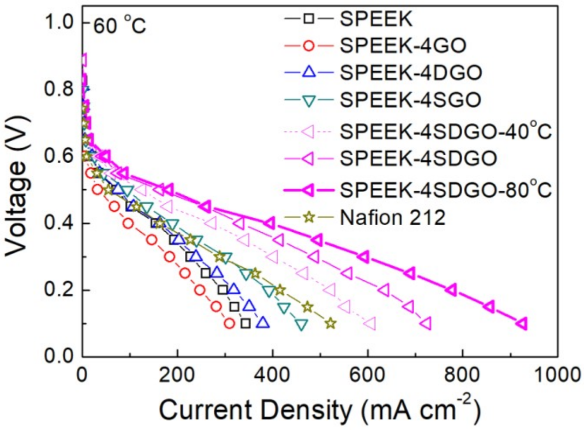


Fig. S7 Polarization curves of DMFCs at 60 °C (unless mentioned otherwise) with 1 M methanol/100% RH O_2.

Supplementary Note 3 Further discussion on the quite different initial OCVs of various DMFCs.

Since we have used the same catalyst layer materials, we think the discrepancy in OCV of the DMFCs based on different membranes are most related to their discrepancy in membrane methanol permeability, as displayed and discussed in Fig. 7c of the main text (1 M methanol, 60 ^{o}C). The initial OCVs of the DMFCs at the beginning of the chemical ASTs (Fig. 8b of the main text) are obviously lower than those in the corresponding polarization curves (Fig. S7), as higher concentration of methanol feed (5 M) and elevated operating temperature during the chemical ASTs (80 ^{o}C) render more severe methanol permeation that causes OCV reduction. Specifically, the most marked initial OCV decrease is observed for the SPEEK-4GO-based DMFC as the severe structual defects and inner voids of SPEEK-4GO membrane demonstrated in the above sections may further enlarge methanol permeation. It is notable that composite PEMs with 4 wt% fillers show an order of SPEEK-4GO>SPEEK-4SGO>SPEEK-4DGO>SPEEK-4SDGO in methanol permeability (Fig. 7c), which translates into the opposite order of their OCVs (Fig. 8b of the main text). However, pristine SPEEK membrane displays some different behaviors. SPEEK possesses lower methanol permeability than SPEEK-4SGO and SPEEK-4DGO (Fig. 7c of the main text), but exhibits lower OCV than SPEEK-4SGO and SPEEK-4DGO (Fig. 8b of the main text). This is because the temperature of the OCV hold (80 ^{o}C) is higher than methanol permeability mesurement (60 ^{o}C). At higher temperature, the pristine SPEEK membrane without the restriction of rigid filler may display the most severe swelling

(Table S4), which is prone to additional enlarge methanol permeability, leading to its degraded OCV. It is also worth pointing out that the difference of the initial OCVs in Fig. 8c is less than that in Fig. 8b, as the concentration of the methanol solution was 1 M in Fig. 8c as compared to 5 M in Fig. 8b.

Table S4 Area swelling[a] and mechanical properties[b] of SPEEK control and composite membranes

Membrane	Area Swelling (%)	Elastic modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
SPEEK	82.5±11.8	666±75	62±9	121±21
SPEEK-4GO	59.7±9.1	737±71	48±11	61±16
SPEEK-4DGO	52.7±6.9	803±69	52±9	75±20
SPEEK-4SGO	58.4±7.8	805±109	68±13	92±19
SPEEK-4SDGO	49.2±6.3	906±59	78±12	109±22
Nafion 212	62.0±8.8	155±18	17±2	234±34

[a] Area swelling was measured at 80 °C in water, well corresponding with the condition in chemical/mechanical ASTs.

[b] Mechanical properties were measured at 23 °C and 50% RH, under the conditions suggested in ASTM D882.

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