## Electronic Supplementary Information

# Graphene oxide – polybenzimidazolium nanocomposite anion exchange membranes for electrodialysis

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#### **1.** Synthetic procedures

#### 1.1. Graphene oxide modification via diazonium chemistry

4-(Trifluoromethylthio)aniline (0.36 mL, 2.48 mmol) and an excess (80 mL) of 1 M HCl were added to a round-bottom flask and the mixture was cooled down to 0-5 °C using an ice-water bath. NaNO<sub>2</sub> (186 mg, 2.69 mmol) was added in one portion and the mixture was allowed to stir for two hours at this temperature. A mixture of graphene oxide (GO) dispersion (62 mL, 248 mg GO) and deionised (DI) water (50 mL) was added dropwise over 15 min and the stirring continued at 0-5 °C for 2 hours. The mixture was allowed to warm up to room temperature and stirred at 20 °C for 20 hours and, finally, 2 hours at 60 °C. The GO was isolated through centrifugation and washed with DI water, methanol and diethyl ether. The modified GO product (235 mg), **mGO-1**, was dried under vacuum.

#### 1.2. Graphene oxide modification via epoxide ring opening

A mixture containing GO dispersion (75 mL, 300 mg GO), DI water (75 mL) and ethanol (75 mL) was sonicated for 20 minutes. To this mixture, in a two-necked round-bottom flask equipped with dropping funnel and reflux condenser, a solution of TFMA (0.88 mL, 6.13 mmol) in ethanol (45 mL) was added and stirred at 80 °C for 20 hours. After the reaction, the ethanol was removed by rotary evaporation. The aqueous suspension remaining was left to stand for 2 hours, following which separation of GO could be observed. The modified GO was filtered on a polyamide membrane filter (0.45  $\mu$ m), then washed multiple times with water, methanol and diethyl ether to remove any excess reagent. The modified GO product (335 mg), **mGO-2** was dried under vacuum.

# **1.3.** Synthesis of poly[2,2'-(*m*-phenylene)-5,5'-bis(*N*,*N*'-dimethylbenzimidazolium)] (PDMBI) iodide

PDMPI was obtained similarly to an earlier reported synthesis but using the much safer  $K_2CO_3$  instead of LiH as base.<sup>1</sup> 77 g of PBI S26 solution (64.8 mmol repeating unit) was diluted with DMAc (300 mL) in a dry two-necked round-bottom flask equipped with dropping funnel and condenser under Ar atmosphere.  $K_2CO_3$  (17.9 g, 129.6 mmol) was added in one portion and deprotonation of the polymer was promoted by stirring the mixture at 70 °C for 2 hours. During this time the amber solution turned into deep red. The mixture was cooled down to 0-5 °C using ice-water bath, then MeI (12.1 mL, 194.4 mmol) was added dropwise over 15 min. The reaction mixture was refluxed at 70 °C for 16 hours during which time a brown precipitate occurred. The precipitate was collected by filtration and washed with DMAc and an excess of water and dried under vacuum to obtain the monomethylated intermediate (**PMBI**, 20.6 g, 95%). To a solution of **PMBI** (5 g, 14.8 mmol) in

DMSO (40 mL), MeI (2 mL, 32.1 mmol) was added in a pressure tube under Ar atmosphere. The tube was sealed and heated to 70 °C, and the reaction mixture was stirred for 24 hours. Then, the mixture was allowed to cool down to room temperature and the product was precipitated by pouring the mixture into 400 mL EtOAc while stirring. The precipitate was collected by filtration and then washed multiple times with ethyl acetate and DI water. The product, the iodide form of **PDMBI** (6.5 g, 71%), was dried under vacuum.

#### 2. X-ray diffraction (XRD)

The XRD pattern was measured over the range 3-100°, using a PANalytical X'Pert Pro (XRD5). Interlayer spacing between GO sheets can be calculated from the diffraction angle of the beam using Bragg's law (Eq. S1):

$$\lambda = 2 \, d \sin \theta \tag{S1}$$

The polymeric material of the membranes has a naturally broad pattern, without any significantly prominent peaks, due to its amorphous nature. There is an increase in intensity of the peak at 26° seen in the patterns of **M2-0.25** and **M2-1**, this peak indicates a slightly increased crystallinity within these nanocomposite structures as a result of hydrogen bonds forming between **mGO-1** and the polymer matrix.<sup>2</sup> At the highest **mGO-1** loading the slightly more intense peak which had formed at 0.25 and 1 wt% **mGO-1** disappears and the XRD pattern appears very similar to that of **M2-0**. This may be the result of nanoparticle overloading resulting in fewer chemical interactions between **mGO-1** and the polymer.<sup>3</sup>



Fig. S1 XRD pattern of mGO-1 compared to unmodified GO (a) and membranes from the M2 series.

#### 3. Raman spectroscopy

Raman spectra were recorded from dry samples using a Renishaw inVia spectrometer. Fig. S2 shows the Raman spectra of unmodified GO, **mGO-1** and **mGO-2**. All spectra display two distinct peaks that correspond to the D band (~1300 cm<sup>-1</sup>) and the G band (~1600 cm<sup>-1</sup>) regions, which are representative of the defects present at the edge of the GO plane and the graphitic structure of GO, respectively.



Fig. S2 Raman spectra of unmodified GO, mGO-1 and mGO-2.

#### 4. Infrared spectroscopy

Fourier-transform infrared spectroscopic analysis (FTIR) of the membranes is shown in Fig. S3. All the spectra are almost identical as expected based on the low **mGO-1** loadings (0-2.5%).



Fig. S3 FTIR spectra of membranes with different mGO-1 loadings.

#### 5. Thermogravimetric analysis (TGA)

TGA was performed on a TGA550 instrument manufactured and supplied by TA Instruments using alumina 100  $\mu$ L pans from the same supplier. All samples were measured using a heating rate of 20 °C min<sup>-1</sup> from 25–800 °C in N<sub>2</sub> atmosphere.



Fig. S4 TGA curves of the membranes showing good thermal stability up to 200-250 °C.

#### 6. Electrodialysis

The electrodialysis experiments were performed on a microBED complete electrodialysis system supplied by PCCell GmbH (Heusweiler, Germany). Pt/Ir-MMO (mixed metal oxide) coated Tistretched metal anode and stainless steel cathode was used. The electrode compartments were separated from the diluate and concentrate compartments with PC-SK CEMs (also from PCCell GmbH). 50 mL 0.05 M Na<sub>2</sub>SO<sub>4</sub> solution was circulated as an electrode wash during the experiment to prevent dangerous cathode reactions. The electrodialysis stack consisted of one concentrate and one diluate compartment separated by an AEM from the M2 series. The active membrane area was 64 cm<sup>2</sup>. Both compartments were filled up with 150 mL 0.1 M NaCl solution prior to the experiment. The NaCl solution was circulated in both compartments and the electrodialysis was carried out for 40 min. The salt concentration of the diluate and concentrate was monitored continuously with a conductivity meter. The electrodialysis was initially carried out with constant current (0.87 A). As the conductivity of the diluate dropped, the voltage to maintain the constant current reached the maximum limit of the electrodialysis stack (24 V). After that point the electrodialysis was continued with constant voltage (24 V). The performances of fabricated membranes were compared in terms of power consumption of salt removal and current efficiency using the following equations:

Power consumption = 
$$\frac{\int U \cdot I dt}{V_{\rm D} \cdot |\Delta C_{\rm D}|}$$
 (S2)

Current efficiency = 
$$\frac{V_{\rm D} \cdot |\Delta C_{\rm D}| \cdot F}{\int I dt}$$
 (S3)

Where U and I are the applied voltage and current, respectively;  $V_D$  is the volume of the diluate (150 mL);  $\Delta C_D$  is the change of salt concentration in the diluate during the electrodialysis; and F is the Faraday constant 96485 C mol<sup>-1</sup>.

#### 7. Zeta potential measurements

In order to determine the surface charge of the membrane samples, zeta potential measurements were performed using an Anton-Paar SurPASS<sup>TM</sup> Electrokinetic Analyzer (with an adjustable gap cell) and the Anton Paar Attract software (version 2.1.5). The gap height of the adjustable gap cell was set to approximately 100 µm for all measurements. A 0.001 M KCl electrolyte solution was passed through the set up by ramping the differential pressure from 0 to 200 mbar. The initial pH of the 0.001 M KCl electrolyte solution was approximately 6.4. To examine the pH dependence of the surface charge, the pH of the electrolyte solution was adjusted using 0.05 M HCl and 0.05 M NaOH solutions. The tests were carried out over a pH range from 4–11. The streaming current values were measured and the zeta potential values were evaluated using the Helmholtz-Smoluchowski approximation. Four zeta potential measurements were performed at each pH value and the average was computed.



Fig. S5 Zeta potential measurements of the M2 membranes in the pH range of 4-11.

#### 8. Anion Exchange Membranes (AEMs)

The data used to prepare Figure 11 are summarised in **Table S1**. The parameters of the commercial AEMs were obtained from the catalogues, safety data sheets or through inquiry from the supplier. The limited number of AEMs in the table from the literature can be explained by the fact that, despite their importance in electromembrane processes, permselectivity and/or area resistance are often not reported. The permselectivity values were calculated in some cases from the reported membrane transport numbers. Although the parameters summarised are correct to the authors' best knowledge, they should be taken with healthy scepticism since the experimental procedures used to obtain them may vary and the error of these values is not known.

Commercial AEMs						
Number	Supplier	Country	Name	Permselectivity	Area Resistance; $R_A$ ( $\Omega$ cm <sup>2</sup> )	$R_{\rm A}^{-1}$ (Ω <sup>-1</sup> cm <sup>-2</sup> )
1			Fumasep <sup>®</sup> FAPQ-375	0.90	2.0	0.500
2		Germany	Fumasep <sup>®</sup> FAB-PK-75	0.95	2.3	0.439
3	Fumatech BWT GmbH		Fumasep <sup>®</sup> FAB-PK-130	0.95	4.0	0.250
4			Fumasep <sup>®</sup> FAD-75	0.88	1.0	1.000
5			Fumasep <sup>®</sup> FAS-50	0.92	1.8	0.556
6			Fumasep® FAA-3-50	0.90	2.5	0.400
7	MEGA a.s.	Czechia	RALEX® AM(H)-PES	0.90	7.5	0.133
8		Japan	Selemion <sup>TM</sup> AMV	0.90	2.8	0.357
9	AGC Engineering Co. Ltd.		Selemion <sup>TM</sup> ASV	0.92	3.7	0.270
10			Selemion <sup>TM</sup> AAV	0.87	6.4	0.156
11			Selemion <sup>™</sup> AHO	0.87	20.0	0.050
12	Guochu	China	TWEDAI	0.95	4.0	0.250
13	Technology Co. Ltd.		TWEDA2	0.95	4.0	0.250
14	VWR International	US	5516428	0.90	2.8	0.357
Membranes reported in the literature						
Number	Reference	Material	Name	Permselectivity	Area Resistance; $R_A$ ( $\Omega$ cm <sup>2</sup> )	$R_{A}^{-1}$ ( $\Omega^{-1}$ cm <sup>-2</sup> )
15	Hosseini et	PVC/ Amberlyst <sup>®</sup> /	<b>S</b> 1	0.87	18.0	0.056
16	16 al., 2014 <sup>4</sup>		S2	0.89	13.0	0.077

Table S1 Commercial AEMs and AEMs recently reported in the literature for electrodialysis.

17	Nemati et al.,	PVC/	S1	0.85	15.0	0.067
18	2015 <sup>5</sup>	TiO2	S2	0.85	11.0	0.091
19		quaternised amine-PSU	M1	0.81	22.0	0.045
20	Duan et al., 2018 <sup>6</sup>		M2	0.83	15.0	0.067
21			M3	0.87	10.0	0.100
22			M4	0.90	6.0	0.167
23			M5	0.94	3.0	0.333
24			NMM-4	0.77	810.0	0.001
25	Khan et al.,	quaternised	NMM-8	0.82	132.0	0.008
26		morpholine-	NMM-12	0.85	7.2	0.139
27	2015	PPO	NMM-15	0.85	4.2	0.238
28			NMM-18	0.90	1.5	0.667
29	Miao et al., 2018 <sup>8</sup>	crosslinked, quaternised	AEM-1	0.79	10.9	0.092
30		amino- PEMA/ PVC/	AEM-2	0.76	11.9	0.084
31		anion exchange resin	AEM-3	0.68	15.9	0.063
32	This work	quaternised PBI/GO	M2-0	0.81	2.9	0.345
33			M2-0.25	0.93	3.8	0.263
34			M2-1	0.99	11.2	0.089
35			M2-2.5	0.93	4.9	0.203



**Fig. S6** Plot showing commercial AEMs and AEMs recently reported in the literature for electromembrane processes.

#### 9. Conductivity – water uptake correlation

Fig. S7 shows the specific conductivity ( $\sigma$ ) of different commercial and reported AEMs as a function of water uptake (WU).  $\sigma$  is often used to characterise AEMs (especially in the field of fuel cells) and it can be easily obtained as a quotient of membrane thickness (*d*) and area resistance ( $R_A$ ):

$$\sigma = d \cdot R_{\rm A}^{-1} \tag{S4}$$

Higher WU is usually associated with higher  $\sigma$ , however no direct correlation can be found for the AEMs summarised in Fig. S7. Most membranes recently reported in the literature failed to keep up with commercial membranes in terms of specific conductivity. The M2 membranes in this work have average specific conductivity, but these values are significantly higher than other reported AEMs with similar water uptake. All M2 membranes exhibit low water uptake of approximately 10%, which is considerably lower than other reported AEMs with similar  $\sigma$  value.



**Fig. S7** Specific conductivity as a function of water uptake for the new, commercial and recently published AEMs for electromembrane processes.

**Table S2** Specific conductivity and water uptake for the new, commercial and recently publishedAEMs for electromembrane processes.

Number	Supplier	Country	Name	Water uptake (%)	Specific conductivity; $\sigma$ (mS cm <sup>-1</sup> )		
	Commercial AEMs						
1	Fumatech	Germany	Fumasep <sup>®</sup> FAB-PK-75	16	3.3		
2			Fumasep <sup>®</sup> FAB-PK-130	14	2.5		
3	D W I CmbH		Fumasep <sup>®</sup> FAS-50	26	5		
4	UIIUII		Fumasep <sup>®</sup> FAA-3-50	19	5		
5	MEGA a.s.	Czechia	RALEX <sup>®</sup> AM(H)-PES	65	8.3		
6	Guochu	China	TWEDAI	35	3.6		
7	Technology Co. Ltd.		TWEDA2	35	3.4		
	AEMs reported in the literature						
Number	Reference	Material	Name	Water uptake (%)	Specific conductivity; $\sigma$ (mS cm <sup>-1</sup> )		
8	Hosseini <i>et</i> <i>al.</i> , 2014 <sup>4</sup>	PVC/ Amberlyst <sup>®</sup> /	S1	47	0.39		
9		PANI	<b>S</b> 2	38	0.54		
10	Nemati <i>et</i> <i>al.</i> , 2015 <sup>5</sup>	Nemati $et = \frac{PVC}{A mberlyct^{\otimes}}$	<b>S</b> 1	48	0.53		
11		5 <sup>5</sup> TiO2	<b>S</b> 2	39	0.73		

12	Duan <i>et al.</i> , 2018 <sup>6</sup>	quaternised amine-PSU	M1	14	0.27
13			M2	20	0.40
14			M3	24	0.60
15			M4	34	1.0
16			M5	44	2.0
17			NMM-4	7	0.011
18	171 1	quaternised morpholine-	NMM-8	10	0.066
19	Knan <i>et al.</i> , $2015^7$		NMM-12	13	1.9
20	2015	PPO	NMM-15	19	3.2
21			NMM-18	28	10.4
22	Miao <i>et al.</i> , 2018 <sup>8</sup>	crosslinked, quaternised	AEM-1	33	0.49
23		amino- PEMA/ PVC/ anion	AEM-2	32	0.61
24		exchange resin	AEM-3	52	0.49
25	This work	quaternised PBI/GO	M2-0	9.4	1.4
26			M2-0.25	10.5	0.97
27			M2-1	9.6	0.29
28			M2-2.5	9.1	0.90

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