



1 Supporting information

- 2 A composite anion conducting membrane based on
- **quaternized cellulose and poly(phenylene oxide) for**
- ⁴ alkaline fuel cell application

5 Dong Ho Kang, Gautam Das, Hyon Hee Yoon* and Il Tae Kim*

6



[Oxalyl chloride]

[1,1,3,3 - tetramethyl urea]

[Guanidine]





7

[Guanidine] [1,6 - diaminohexane]

[Di - guanidine]

- 8 **Scheme S1.** Synthesis of guanidine and di-guanidine
- 9

10 **Table S1.** Composition in various membrane samples

Membrane	qPPO, g	D-Cel, g	DG-Cel, g
qPPO	1	-	-
qPPO/D-Cel3	1	0.03	-
qPPO/D-Cel5	1	0.05	-
qPPO/D-Cel7	1	0.07	-
qPPO/D-Cel10	1	0.10	-
qPPO/D-Cel15	1	0.15	-
qPPO/DG-Cel3	1	-	0.03
qPPO/DG-Cel5	1	-	0.05
qPPO/DG-Cel7	1	-	0.07
qPPO/DG-Cel10	1	-	0.10
qPPO/DG-Cel15	1	-	0.15



16

17 Figure S1. ¹H-NMR spectra of (a) DG, (b) Cel, (c) t-Cel, (d) D-Cel, (e) DG-Cel, (f) PPO, (g) bPPO, and 18 (h) qPPO.



Figure S2. SEM images of (a) Cel, (b) t-Cel, (c) D-Cel, and (d) DG-Cel.



Polymers 2020, 12, x FOR PEER REVIEW

Table S2. Elemental analysis of D-Cel and DG-Cel

Name	N (%)	C (%)	H (%)
D-Cel	5.19	47.91	6.825
DG-Cel	3.49	32.76	5.227









33 **Table S3.** Comparative data of AEMs

Membrane	IC (RT), mS/cm	IC (>RT), mS/cm	IEC, mmol g ⁻¹	WU, %	Ref.
PAES	~ 30	107 (80 °C)	2.2	50~60	[1]
Im-SiO ₂ /TA-PPO	~ 40	105 (80 °C)	3.15	145	[2]
PAES/Nano-ZrO ₂	23.1	36.5 (80 °C)	1.82	28.1	[3]
CLQCPAES/nano-ZrO2	16.2	55.2 (80 °C)	1.23	56.2	[4]
PSf/MMT	~ 15	47.3 (95 °C)	1.21	< 50	[5]
CS/QHNTs	5.56	17 (90 °C)	~0.4	79.2	[6]
QPSfDMC2	54	94 (70 °C)	2.34	124.72	[7]
QPPOQGO2	90.9	151 (80 °C)	2.25	74.28	[8]
QPSfQC15	74	128 (80 °C)	2.71	80.47	[9]
BG-BPS/PTFE	31	65 (60 °C)	1.14	29.4	[10]
Tri-QPESOH	45.9	130.9 (80 °C)	2.31	62	[11]
qPPO/D-Cel7	58.9	108.2 (70 °C)	1.66	67	This Work
qPPO/DG-Cel7	87.5	164.7 (70 °C)	1.24	91	This Work

34 * PAES = Poly(arylene ether sulfone), Im-SiO2/TA-PPO = Imidazolium-modified silica/Triple-ammonium side chain poly(phenylene oxide), CLQCPAES = Cross-linked

35 multiblockcopoly(arylene ether sulfone), PSf = polysulfone, MMT = montmorillonite, CS = chitosan, QHNTs = Quaternized halloysite nanotubes, QPSfDMC = quaternized poly(sulfone)

36 with N,N-dimethyl chitosan, QPPOQGO = quaternized poly(phenylene oxide) with modified graphene oxide, QPSfQC = DABCO polysulfone DABCO cellulose, BG-BPS = Bi-

37 guanidinium bridged polysilsesquioxane, PTFE = poly tetra fluoro ethylene, QPESOH = quaternized poly (ether sulfone)



42 Table S4. Comparative data of direct urea	ı fuel cell
---	-------------

Membrane	Fuel, Electrolyte	Catalyst (Anode-Cathode)	Power density (mW cm-2)	Ref
AMI-7001	0.33 mol L ⁻¹ Urea,	*Gr/Ni – Pt/C	4.06 x 10 ⁻³	[12]
	1 mol L ⁻¹ KOH		(Room temperature)	
Astom ACS A-	0.5 mol L ⁻¹ Urea	CuNi^PEDOT*PSS – Pt- B	1.88	[13]
5152			(Room temperature)	
FAA-3-50,	0.33 mol L ⁻¹ Urea,	$Pd_Ni/C - Pd/C$	1.12	[14]
Fumapem	1 mol L ⁻¹ KOH	1 u = 1 u / c	(Room temperature)	[14]
Fumasep FAA-3-	0.33 mol L ⁻¹ Urea,	Ni/C –	0 4226 (50 °C)	[15]
50	1 mol L ⁻¹ KOH	Mn ₃ O ₄ -Co ₃ O ₄ /MWCNT	0.4220 (50 °C)	[15]
QPSfDMC2	0.33 mol L ⁻¹ Urea,	$N_{\rm H}/C = P_{\rm T} R_{11}/C$	$44(70 \circ C)$	[7]
	1 mol L ⁻¹ KOH	$1 \times 1/C = 1 \times 1/C$	4.4 (70°C)	[7]
QPPOQGO2	0.33 mol L ⁻¹ Urea,	$N_{i}/C = P_{i}P_{11}/C$	52(60°C)	[8]
	1 mol L ⁻¹ KOH	$1 \times 1/C = 1 \times 1/C$	5.2 (00°C)	[0]
qPPO/D-Cel7	0.33 mol L ⁻¹ Urea,	Ni/C P+P11/C	8 36 (70 °C)	This
	3 mol L ⁻¹ KOH	$1 \times 1/C = 1 \times 1/C$	0.50(70 C)	work
qPPO/DG-Cel7	0.33 mol L ⁻¹ Urea,	N_{i}/C $P_{i}P_{11}/C$	12 25 (70 °C)	This
	3 mol L ⁻¹ KOH	$1 \times 1/C = 1 \times 1/C$	12.23(70 C)	work

* Gr = graphene, MWCNT = multiwalled carbon nanotubes, AG = aerogel, PEDOT*PSS = poly(3,4-ethylenedioxythiophene) polystyrene sulfonate, Pt-B = Pt-Black

45 **References**

- Lee, K.H.; Cho, D.H.; Kim, Y.M.; Moon, S.J.; Seong, J.G.; Shin, D.W.; Sohn, J.Y.; Kim, J.F.; Lee, Y.M. Highly
 conductive and durable poly(arylene ether sulfone) anion exchange membrane with end-group cross linking. *Energy Environ. Sci.* 2017, *10*, 275–285, doi:10.1039/c6ee03079c.
- Chen, N.; Long, C.; Li, Y.; Wang, D.; Zhu, H. A hamburger-structure imidazolium-modified
 silica/polyphenyl ether composite membrane with enhancing comprehensive performance for anion
 exchange membrane applications. *Electrochim. Acta* 2018, *268*, 295–303, doi:10.1016/j.electacta.2018.01.064.
- 52 3. Li, X.; Yu, Y.; Meng, Y. Novel quaternized poly(arylene ether sulfone)/nano-ZrO2 composite anion
 53 exchange membranes for alkaline fuel cells. ACS Appl. Mater. Interfaces 2013, 5, 1414–1422,
 54 doi:10.1021/am302844x.
- Li, X.; Tao, J.; Nie, G.; Wang, L.; Li, L.; Liao, S. Cross-linked multiblock copoly(arylene ether sulfone)
 ionomer/nano-ZrO2 composite anion exchange membranes for alkaline fuel cells. *RSC Adv.* 2014, *4*, 41398–
 41410, doi:10.1039/c4ra06519k.
- Liao, X.; Ren, L.; Chen, D.; Liu, X.; Zhang, H. Nanocomposite membranes based on quaternized polysulfone
 and functionalized montmorillonite for anion-exchange membranes. *J. Power Sources* 2015, 286, 258–263,
 doi:10.1016/j.jpowsour.2015.03.182.
- 6. Shi, B.; Li, Y.; Zhang, H.; Wu, W.; Ding, R.; Dang, J.; Wang, J. Tuning the performance of anion exchange
 membranes by embedding multifunctional nanotubes into a polymer matrix. *J. Memb. Sci.* 2016, 498, 242–
 253, doi:10.1016/j.memsci.2015.10.005.
- Das, G.; Kim, C.Y.; Kang, D.H.; Kim, B.H.; Yoon, H.H. Quaternized polysulfone cross-linked N,N-dimethyl
 chitosan-based anion-conducting membranes. *Polymers* (*Basel*). 2019, 11, 23–27,
 doi:10.3390/polym11030512.
- Bas, G.; Dongho, K.; Kim, C.Y.; Yoon, H.H. Graphene oxide crosslinked poly(phenylene oxide)
 nanocomposite as high-performance anion-conducting membrane. J. Ind. Eng. Chem. 2019, 72, 380–389,
 doi:10.1016/j.jiec.2018.12.040.
- Das, G.; Park, B.J.; Yoon, H.H. A bionanocomposite based on 1,4-diazabicyclo-[2.2.2]-octane cellulose nanofiber cross-linked-quaternary polysulfone as an anion conducting membrane. *J. Mater. Chem. A* 2016, 4, 15554–15564, doi:10.1039/c6ta05611c.
- Qu, C.; Zhang, H.; Zhang, F.; Liu, B. A high-performance anion exchange membrane based on biguanidinium bridged polysilsesquioxane for alkaline fuel cell application. *J. Mater. Chem.* 2012, 22, 8203– 8207, doi:10.1039/c2jm16211c.
- Chen, W.; Yan, X.; Wu, X.; Huang, S.; Luo, Y.; Gong, X.; He, G. Tri-quaternized poly (ether sulfone) anion
 exchange membranes with improved hydroxide conductivity. *J. Memb. Sci.* 2016, 514, 613–621,
 doi:10.1016/j.memsci.2016.05.004.
- Yousef, A.; El-Newehy, M.H.; Al-Deyab, S.S.; Barakat, N.A.M. Facile synthesis of Ni-decorated multi-layers
 graphene sheets as effective anode for direct urea fuel cells. *Arab. J. Chem.* 2017, *10*, 811–822,
 doi:10.1016/j.arabjc.2016.12.021.
- Kaneto, K.; Nishikawa, M.; Uto, S.; Osawa, T. Direct urea fuel cells based on CuNi plated cloth as anode
 catalyst. *Chem. Lett.* 2018, 47, 1285–1287, doi:10.1246/cl.180566.
- Yoon, J.; Lee, D.; Lee, Y.N.; Yoon, Y.S.; Kim, D.J. Solid solution palladium-nickel bimetallic anode catalysts
 by co-sputtering for direct urea fuel cells (DUFC). *J. Power Sources* 2019, 431, 259–264,
 doi:10.1016/j.jpowsour.2019.05.059.
- Ngoc, T.; Pham, T.; Yoon, Y.S. Multiwalled Carbon Nanotubes for Cathode Catalyst in Urea Fuel Cell. 2020,
 1–13.
- 89