© 2021 Wiley-VCH GmbH



Supporting Information

for Adv. Funct. Mater., DOI: 10.1002/adfm.202102080

Aramid Nanofiber Membranes for Energy Harvesting from Proton Gradients

Cheng Chen, Guoliang Yang, Dan Liu,* Xungai Wang, Nicholas A. Kotov,* and Weiwei Lei*

Copyright 2021 Wiley-VCH GmbH

Supporting Information

Aramid Nanofiber Membranes for Energy Harvesting from Proton Gradients

Cheng Chen,^{1,2} Guoliang Yang,¹ Dan Liu,^{1,*} Xungai Wang,¹ Nicholas A Kotov^{3,4,5,6,*} and Weiwei Lei^{1,*}

Dr. C. Chen, Dr. G. Yang, Dr. D. Liu, Prof. X. Wang, Dr. W. Lei. Institute for Frontier Materials, Deakin University, Locked Bag 2000, Geelong, Victoria 3220, Australia E-mail: dan.liu@deakin.edu.au; weiwei.lei@deakin.edu.au

Dr. C. Chen

School of Resources and Environment, Anhui Agricultural University, 130 Changjiang West Road, Hefei, 230036, Anhui, China

Prof. N. A. Kotov

Department of Chemical Engineering, University of Michigan, Ann Arbor, Michigan 48109, United States; Department of Biomedical Engineering, University of Michigan, Ann Arbor, Michigan 48109, United States; Department of Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan 48109, United States; Biointerfaces Institute, University of Michigan, Ann Arbor, Michigan 48109, United States E-mail: kotov@umich.edu



Figure S1. TEM images of the individual ANFs. The inset in the bottom shows a single aramid nanofiber.



Figure S2. SEM images of the ANF membrane. The scale bars are $1\mu m$ (A) and 200 nm (B).



Figure S3. Representative photograph of the ANF membrane after soaking in 1 M HCl for one week.



Figure S4. FTIR spectra of ANF membranes after treatment with 1M solutions of HCl, H_2SO_4 , and NaCl for one week.



Figure S5. Raman scattering spectra of ANF membranes after one-week treatment with 1M solutions of HCl, H_2SO_4 , and NaCl.



Figure S6. Zeta potential of the ANFs membrane in KCl.



Figure S7. The continuous energy output.

Table S1. The cation selectivity caclulation for the ioninc transport through ANF membranes.

Electrolyte	$\begin{array}{c} C_1 \\ \left(M \right)^a \end{array}$	C _h (M)	E _{redox} (mV)	Ezero-current voltage (mV)	E _{osmotic} (mV)	S _{selectivity}	t ⁺
HC1	0.001	1	180	300	120	0.677	0.838
KCl	0.001	1	155	196	41	0.232	0.616

a: M means molL⁻¹.

Table S2. The specific values of maximum power output of ANF membranes in various electrolytes. a: M means molL⁻¹.

Electrolyte	Concentration (M) ^a	R _{max} (kΩ)	P _{max} (W m ⁻²)
HCl	10 ⁻³ - 1	47	17.28
KCl		200	2.35
H_2SO_4		100	1.06
H ₃ PO ₄		100	0.70

Table S3. Elaboration of different electrochemical contributions to the concentration energy harvesting device.

Electrolyte	I _{measured} (µA)	7.6
	I _{redox} (μA)	4.4
	I _{osmotic} (µA)	3.2
	V _{measured} (mV)	310
HCl (10 ⁻³ -1 molL ⁻¹)	V _{redox} (mV)	180
(10 Those)	V _{osmotic} (mV)	130
	P _{calculated} (Wm ⁻²)	19.6
	Posmotic (Wm ⁻²)	3.5

Table S4. The comparison of various membranes with different active areas for osmotic energy harvesting.

Membrane	Thickness (µm)	Electrolyte	Power (W m ⁻²)	Active area Region	Working time	Ref.
single-layer molybdenum disulfide	0.65 nm	0.001-1.0 M KCl	10 ⁶	nm x nm	1 h	1
BNNT	1	0.001-1.0 M KCl	4000	nm x nm	/	2
Conical Pores	12	0.001-0.5 M KCl	945	μm x μm	/	3
PES-Py/HS20	11	0.01-5.0 M NaCl	5.1	μm x μm	120 h	4
MXene/Kevlar	4.5	0.01-0.5 M NaCl	4.1	μm x μm	32 d	5
ionic diode membrane (mesoporous carbon and macroporous alumina)	$4.2 + 60^{a}$	0.01-0.5 M NaCl	3.46	µm x µm	/	6
Polymer/Graphe ne Oxide	1 + 30 ^b	0.01-0.5 M NaCl	0.76	μm x μm	/	7
Fumasep FAD and FKD	82	0.01-0.5 M NaCl	0.7	cm x cm	/	8
FKS as CEM and FAS as AEM (Stacks of anion	30-40	0.01-0.5 M NaCl	1.2	cm x cm	/	9

and cation exchange membranes)						
Charged Graphene oxide membrane pairs	10	0.01-0.5 M NaCl	0.77	mm x mm	16 h	10
ABN	1	0.01-0.5 M NaCl	0.40	mm x mm	200 h	Joule
ANFs	10	0.001-1 .0 M HC1	17.3	0.03 mm x mm	240 h	This work
ANFs	10	0.001-1 .0 M HCl	1.02	3.14 mm x mm	4 h	This work
ANFs	10	0.001-1. 0 M HC1	0.20	19.625 mm x mm	4 h	This work
ANFs	10	0.001-1 .0 M HCl	0.16	78.5 mm x mm	4 h	This work

Note: a: 2-µm-thick MesoClayer is attached on the top of a 60-µm-thick MacroA substrate.

b: 1 μm PPSU-Pyx was casted on 30 μm GO membrane.

Table S5. Maximum power output of ANF membranes in HCl solution under various temperatures.

Electrolyte	Temperature (K)	R _{max} (kΩ)	P _{max} (W m ⁻²)
	298	47	17.28
HCI (10 ⁻³ -1 M)	323	12	63
	343	12	77

References

1. Feng, J.; Graf, M.; Liu, K.; Ovchinnikov, D.; Dumcenco, D.; Heiranian, M.; Nandigana, V.; Aluru, N. R.; Kis, A.; Radenovic, A., Single-layer MoS 2 nanopores as nanopower generators. Nature **2016**, 536 (7615), 197.

2. Siria, A.; Poncharal, P.; Biance, A.-L.; Fulcrand, R.; Blase, X.; Purcell, S. T.; Bocquet, L., Giant osmotic energy conversion measured in a single transmembrane boron nitride nanotube. Nature **2013**, 494 (7438), 455.

3. Lin, C.-Y.; Combs, C.; Su, Y.-S.; Yeh, L.-H.; Siwy, Z. S., Rectification of Concentration Polarization in Mesopores Leads To High Conductance Ionic Diodes and High Performance Osmotic Power. Journal of the American Chemical Society **2019**, 141 (8), 3691-3698.

4. Zhu, X.; Hao, J.; Bao, B.; Zhou, Y.; Zhang, H.; Pang, J.; Jiang, Z.; Jiang, L., Unique ion rectification in hypersaline environment: A high-performance and sustainable power generator system. Science advances **2018**, 4 (10), eaau1665.

5. Zhang, Z.; Yang, S.; Zhang, P.; Zhang, J.; Chen, G.; Feng, X., Mechanically strong MXene/Kevlar nanofiber composite membranes as high-performance nanofluidic osmotic power generators. Nature communications **2019**, 10 (1), 2920.

6. Gao, J.; Guo, W.; Feng, D.; Wang, H.; Zhao, D.; Jiang, L., High-performance ionic diode membrane for salinity gradient power generation. Journal of the American Chemical Society **2014**, 136 (35), 12265-12272.

7. Zhu, X.; Zhou, Y.; Hao, J.; Bao, B.; Bian, X.; Jiang, X.; Pang, J.; Zhang, H.; Jiang, Z.; Jiang, L., A charge-density-tunable three/two-dimensional polymer/graphene oxide heterogeneous nanoporous membrane for ion transport. ACS nano **2017**, 11 (11), 10816-10824.

8. Veerman, J.; Saakes, M.; Metz, S. J.; Harmsen, G. J., Reverse electrodialysis: Performance of a stack with 50 cells on the mixing of sea and river water. Journal of Membrane Science **2009**, 327 (1-2), 136-144.

9. Vermaas, D. A.; Saakes, M.; Nijmeijer, K., Doubled power density from salinity gradients at reduced intermembrane distance. Environmental science & technology **2011**, 45 (16), 7089-7095.

10. Ji, J.; Kang, Q.; Zhou, Y.; Feng, Y.; Chen, X.; Yuan, J.; Guo, W.; Wei, Y.; Jiang, L., Osmotic power generation with positively and negatively charged 2D nanofluidic membrane pairs. Advanced Functional Materials **2017**, 27 (2), 1603623.