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SUPPLEMENTARY INFORMATION

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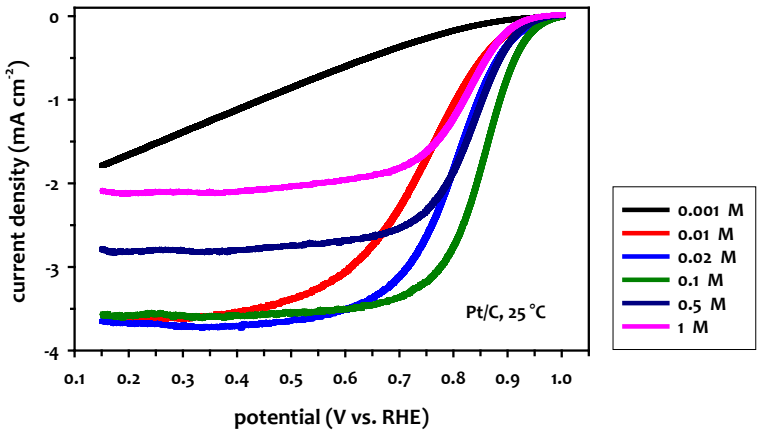
Highly quaternized polystyrene ionomers for high performance anion exchange membrane water electrolysers

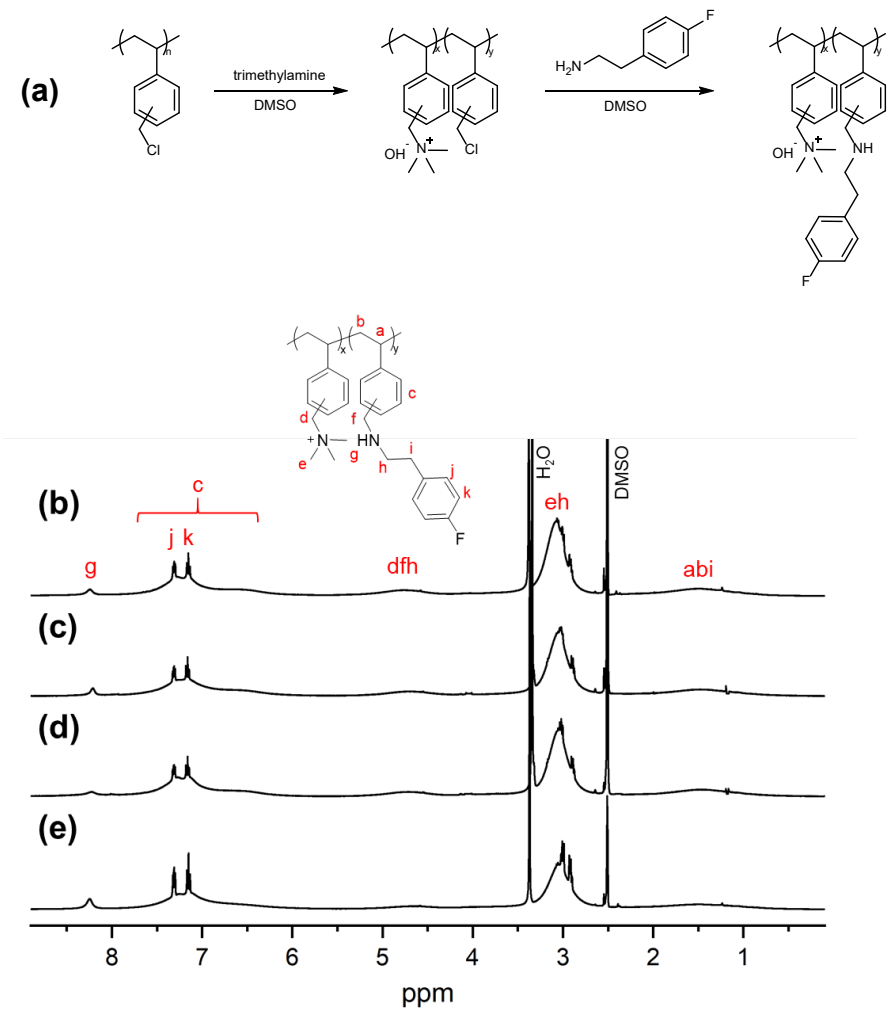
Dongguo Li[1,5], Eun Joo Park[1,5], Wenlei Zhu[2,5], Qiurong Shi[2], Yang Zhou[2], Hangyu Tian[2], Yuehe Lin[2]✉, Alexey Serov[3], Barr Zulevi[3], Ehren Donel Baca[4], Cy Fujimoto[4], Hoon T. Chung[1] and Yu Seung Kim[1]✉

[1]MPA-11: Materials Synthesis and Integrated Devices, Los Alamos National Laboratory, Los Alamos, New Mexico, USA. [2]School of Mechanical and Materials Engineering, Washington State University, Pullman, Washington, USA. [3]Pajarito Powder LLC, Albuquerque, New Mexico, USA. [4]Nanoscale Sciences Department, Sandia National Laboratories, Albuquerque, New Mexico, USA. [5]These authors contributed equally: Dongguo Li, Eun Joo Park, Wenlei Zhu. ✉e-mail: yuehe.lin@wsu.edu; yskim@lanl.gov

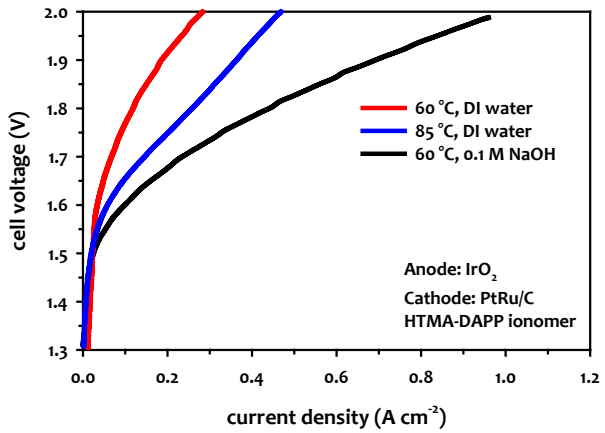
Supplementary Figures.



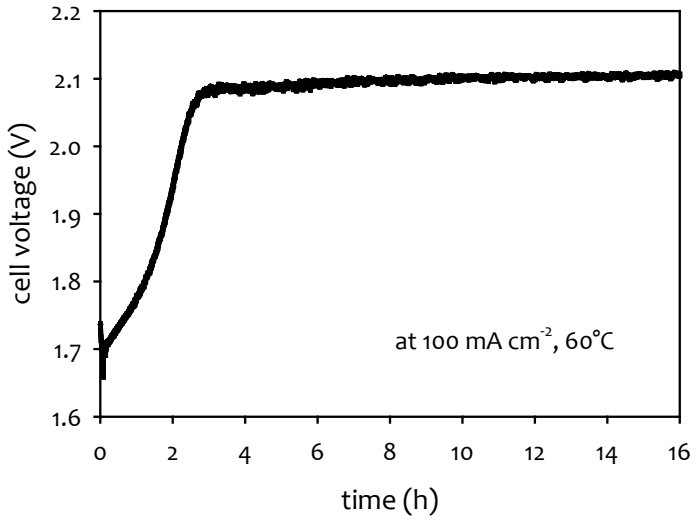
Supplementary Fig. 1 | Impact of NaOH concentration on activities of electrocatalysts. ORR activity of Pt/C. All curves were recorded at room temperature with a 10 mV/s scan rate. The ORR polarization curves were recorded at 1600 rpm with *iR* drop correction.



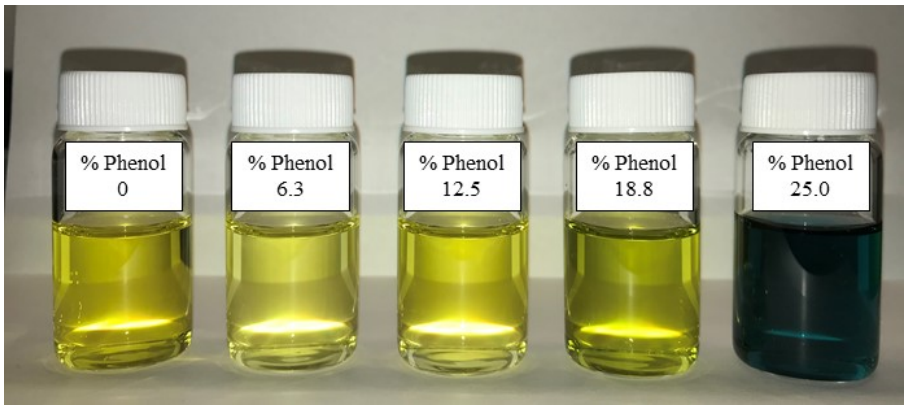
Supplementary Fig. 2 | Synthesis of quaternized polystyrene (TMA-*x*) ionomer. a, Synthetic scheme of TMA-x. **b-e**, ^{1}H NMR of the TMA-70 (IEC = 3.3 mequiv. g^{-1}) (**b**), TMA-62 (IEC = 2.9 mequiv. g^{-1}) (**c**), TMA-53 (IEC = 2.6 mequiv. g^{-1}) (**d**), and TMA-45 (IEC = 2.2 mequiv. g^{-1}) in DMSO-d$_6$ (**e**).



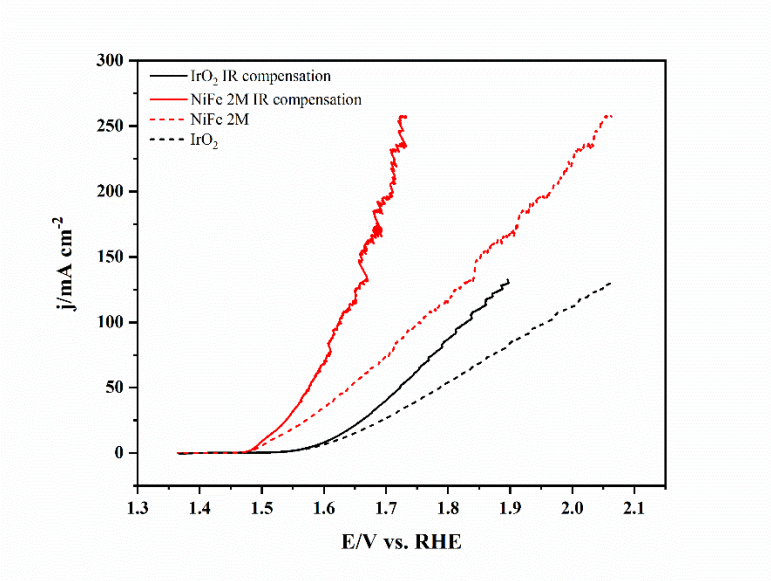
Supplementary Fig. 3 | The performance of MEA employing the control HTMA-DAPP ionomer. The performance was measured at 60 and 85 °C; AEM: HTMA-DAPP (26 μm thickness); anode: IrO_2 (2.5 mg cm^{-2}), cathode: PtRu/C (50% Pt, 25% Ru wt., 2 mg_{Pt} cm^{-2}).



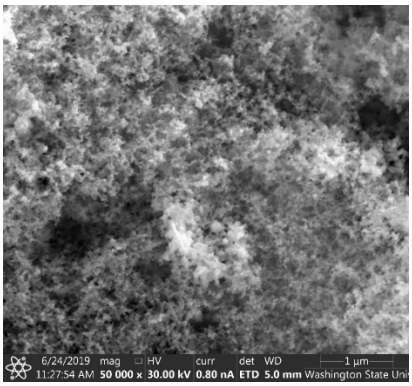
Supplementary Fig. 4 | Cell voltage change of pure water-fed AEM electrolyzer. AEM: HTMA-DAPP, 26 μm thick, ionomer: HTMA-DAPP, anode: IrO_2 (2.5 mg cm^{-2}), cathode: PtRu/C (50% Pt, 25% Ru wt., 2 mg_{Pt} cm^{-2}). Measured the performance at 60 °C under constant current density of 100 mA cm^{-2}.

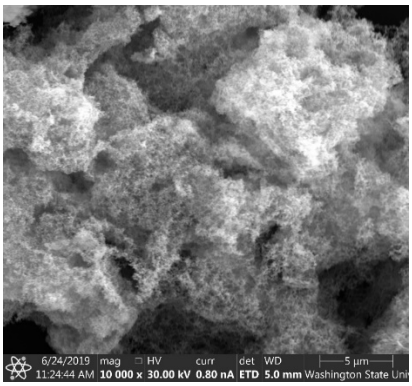


Supplementary Fig. 5. | pH change of the 1.6 M TMAOH solution as a function of phenol concentration. Indigo Carmine (pH >13: yellow, pH <11 : blue) was used as a pH indicator.

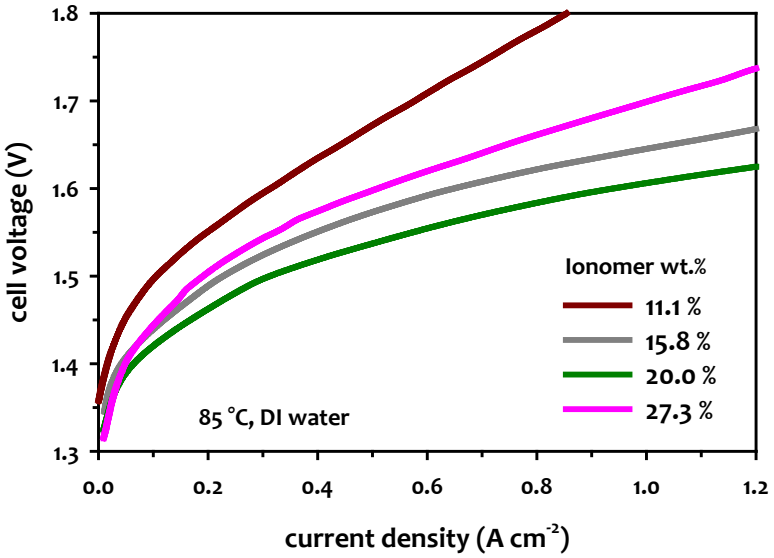


Supplementary Fig. 6 | OER curves of Ni_2Fe_1 catalysts and commercial IrO_2 in 1 M KOH solution. scan rate of 5 mV s^{-1} and rotation rate of 1600 rpm before and after iR compensation.

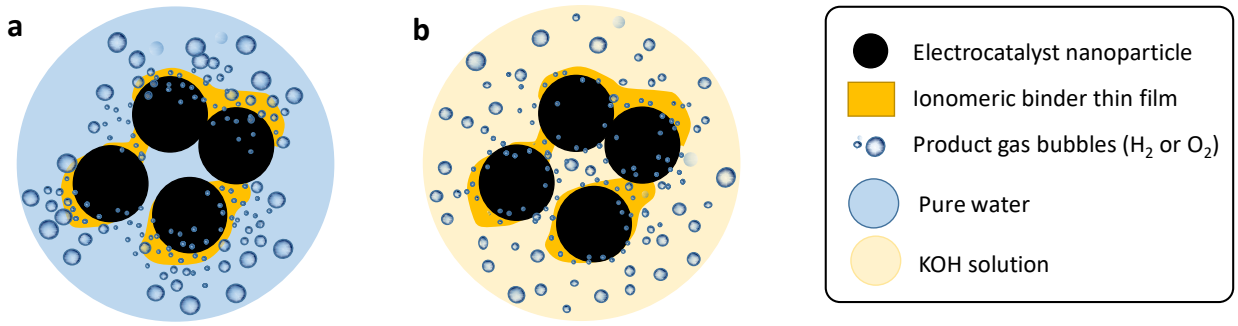




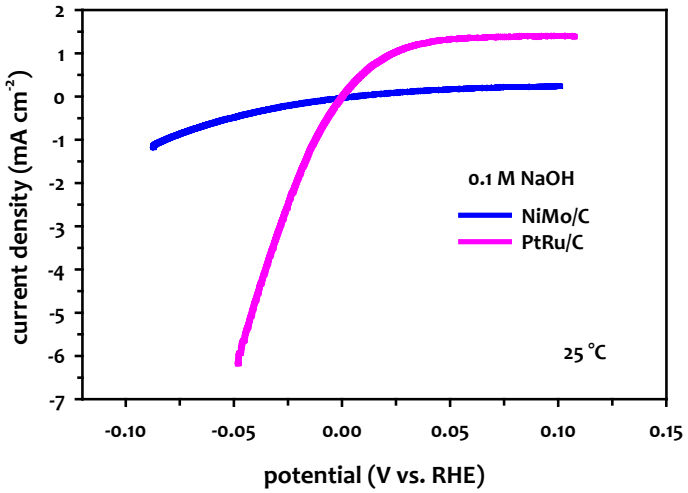
Supplementary Fig. 7 | SEM images of Ni_2Fe_1 nanofoams.



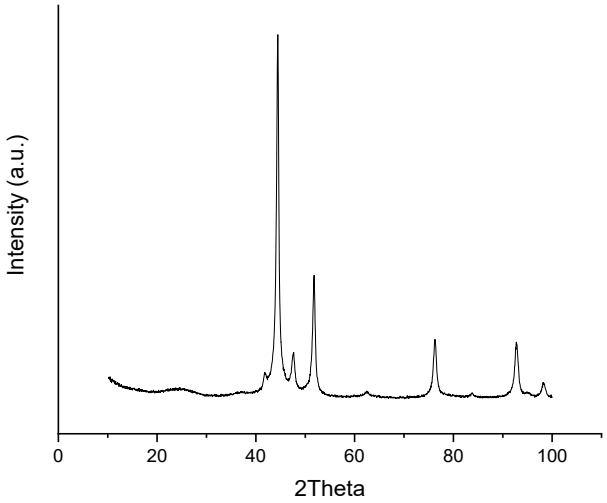
Supplementary Fig. 8 | The impact of ionomer content on electrolyzer performance. The performance of MEA employing a NiFe nanofoam (3 mg_{metal} cm^{-2}) OER and Pt-Ru/C (50 wt.% Pt, 25 wt.% Ru, 2 mg_{Pt} cm^{-2}) HER catalysts, TMA-70 ionomer and HTMA-DAPP AEM (26 μm thickness). The performance was measured at 85 °C at ambient pressure with pure water flowing to the anode.



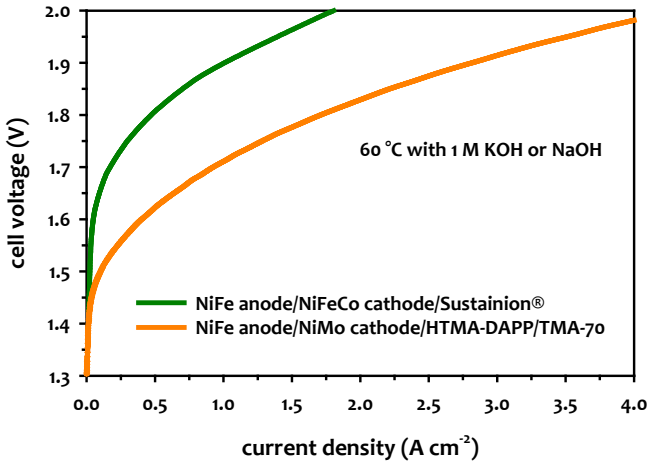
Supplementary Fig. 9 | The schematic illustration of water mass transport. **a,** pure water-fed electrode and **b,** KOH solution-fed electrode. The gas evolving in the pure water-fed electrode is non-uniform due to localized ionomer-catalyst interface, while the gas evolving in the KOH solution-fed electrode is uniform since the KOH solution further leaches to the electrochemically active catalyst surface.



Supplementary Fig. 10 | The HER/HOR voltammogram comparison between NiMO/C and PtRu/C. NiMo/C (39 μg) and PtRu/C (50 wt.% Pt, 25 wt.% Ru, 25 wt.% C) (5 μg) in H_2 saturated 0.1 M NaOH at the scan rate of 5 mV s^{-1}. The HER/HOR curves were corrected by *i*R drop.



Supplementary Fig. 11 | XRD of NiMo catalysts. The XRD pattern on Ni_9Mo_1/KB is quite similar to previously reported data.[1] The main phase in the synthesized sample is $Ni_{87}Mo_{13}$, which is close to expected. The crystallites size is close to 13 nm, which is relatively small taking into account high loading of metals (50 wt.% loading of Ni_9Mo_1 on KetjenBlack).



Supplementary Fig. 12 | The performance comparison of Sustainion®-based[2] and TMA-70-based MEAs in 1 M alkaline solution and at 60 °C. Sustainion®-based MEA: NiFe anode and NiFeCo cathode (performance measured in 1 M KOH). TMA-70-based MEA: NiFe anode and NiMo cathode (performance measured in 1 M NaOH).

Supplementary Tables

Supplementary Table 1. | Ionomer properties.

Ionomer	Theoretical IEC (mequiv. g^{-1})	Experimental IEC[a] (mequiv. g^{-1})	Ion conductivity[b] (mS cm^{-1})
TMA-70	3.3	3.3	8.7
TMA-62	2.9	2.9	8.1
TMA-53	2.4	2.6	7.4
TMA-45	2.0	2.2	6.1

[a] The average IEC value of two samples determined by Mohr titration. [b] Solution conductivity (Cl^- form) was measured at TMA = 0.36 M in water at 80 °C.

Supplementary Table 2. | pH and conductivity of the TMAOH and phenol mixture at 25 °C.

% phenol formation on backbone	pH	Conductivity (mS/cm)
0	14.2	165
6.3	14.1	123
12.5	14.0	85
18.8	13.4	39
25	11.4	25
31.3	11.0	24

References

1 Kabir, S. *et al.* Platinum group metal-free NiMo hydrogen oxidation catalysts: high performance and durability in alkaline exchange membrane fuel cells. *J. Mater. Chem. A* **5**, 24433-24443 (2017).

2 Kaczur, J. J., Yang, H. Z., Liu, Z. C., Sajjad, S. A. & Masel, R. I. Carbon dioxide and water electrolysis using new alkaline stable anion membranes. *Front. Chem.* **6,** 263 (2018).