Supplementary Information

Yolk-shell structured microsphere consisting of CoO/CoP hetero-interfaced nanocomposite as highly active hydrogen evolution reaction electrocatalysts for AEM electrolyzer stacks

In Tae Kim[a,c], Tae Ha Kim[a,c], Seong Jun Moon[b], Gi Dae Park[a,b*], Yoo Sei Park[a,b*]

AUTHOR ADDRESS.

[a] Department of Urban, Energy, and Environmental Engineering, Chungbuk National University, Chungdae-ro 1, Seowon-Gu, Cheongju, Chungbuk, 28644 Republic of Korea

[b] Department of Urban, Energy, and Environmental Engineering, Chungbuk National University, Chungdae-ro 1, Seowon-Gu, Cheongju, Chungbuk, 28644 Republic of Korea

[c] These authors contributed equally to this work.

Corresponding author

Prof. Gi Dae Park : gdpark@chungbuk.ac.kr

Prof. Yoo Sei Park : yspark@chungbuk.ac.kr

E-mail:

Prof. Gi Dae Park : gdpark@chungbuk.ac.kr

Prof. Yoo Sei Park : yspark@chungbuk.ac.kr

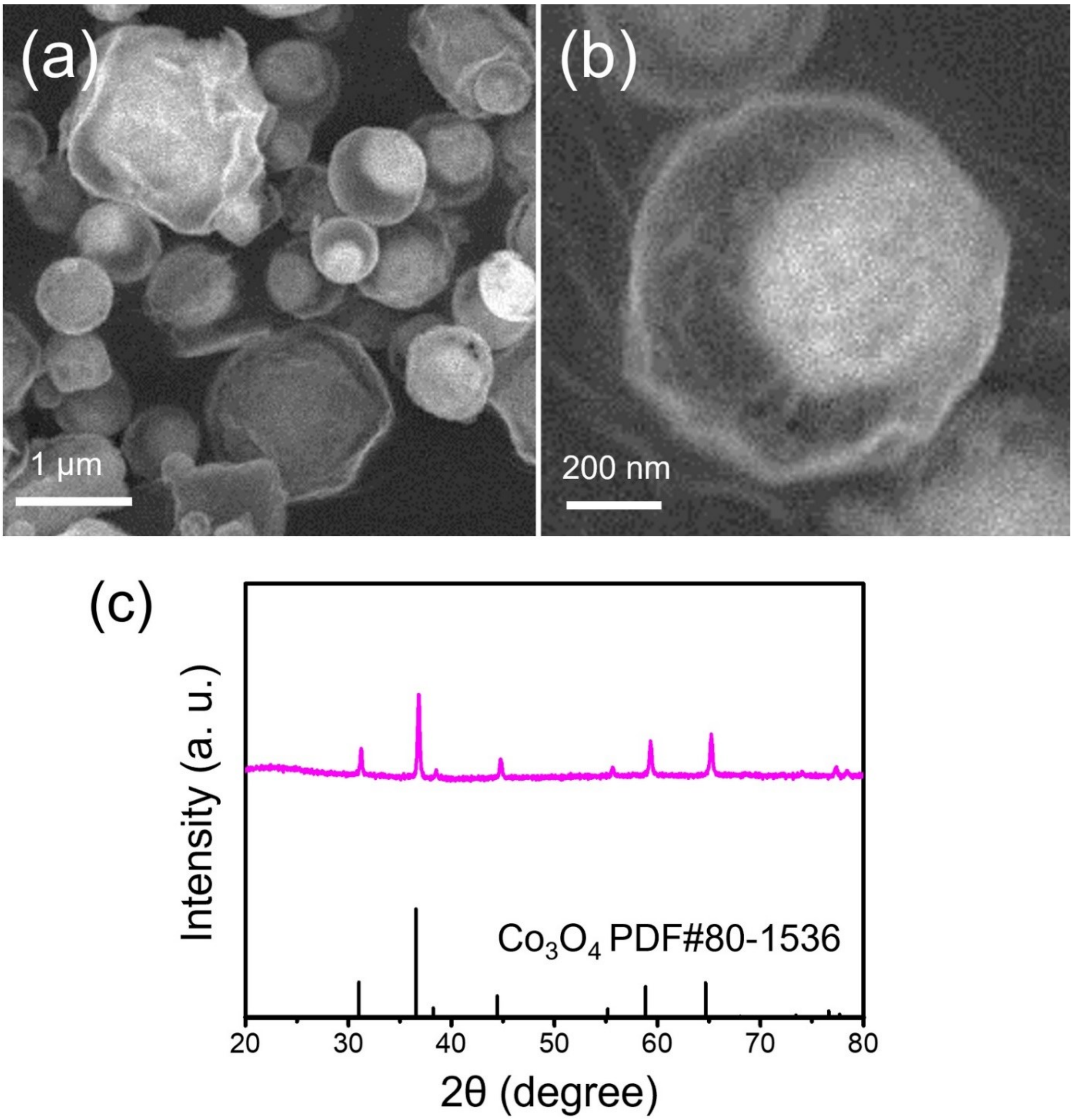

Figure S1. (a-b) SEM images and (c) XRD pattern of YS-Co_3O_4.

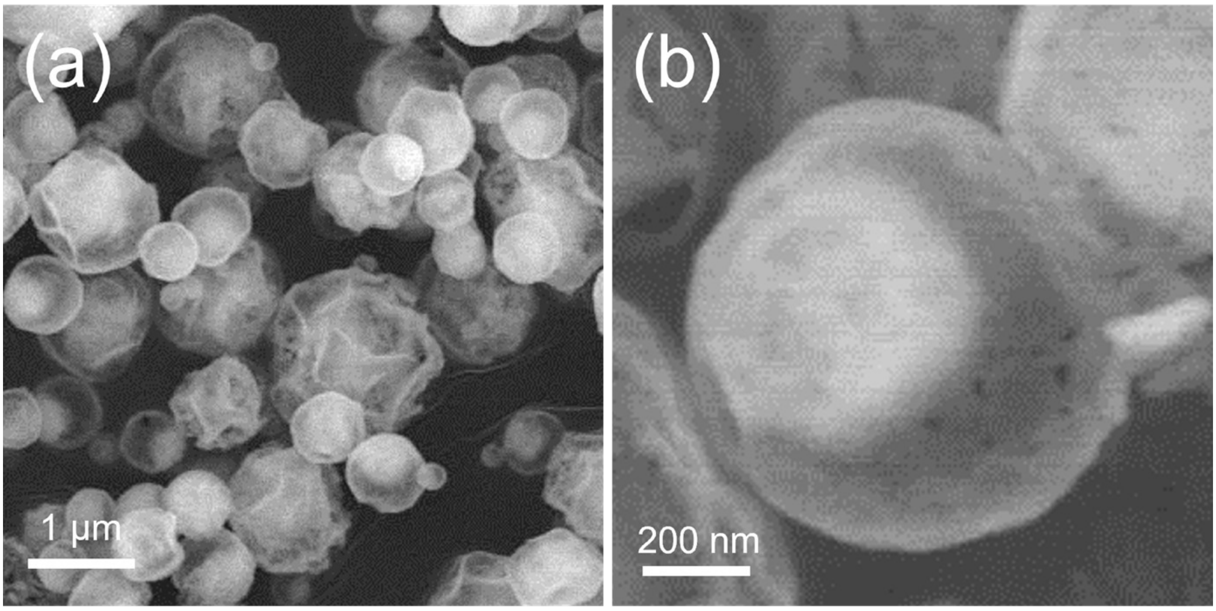

Figure S2. SEM images of YS-CoO.

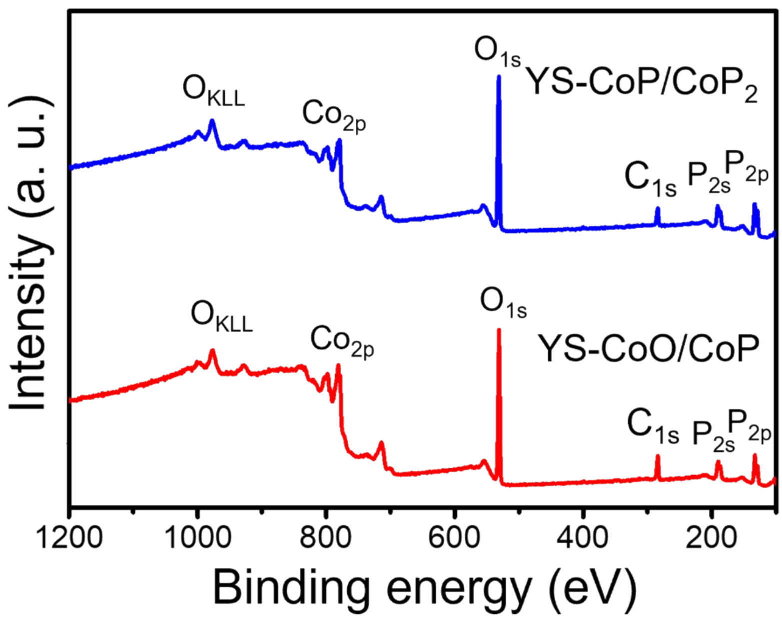

Figure S3. Full scan XPS survey spectrum.

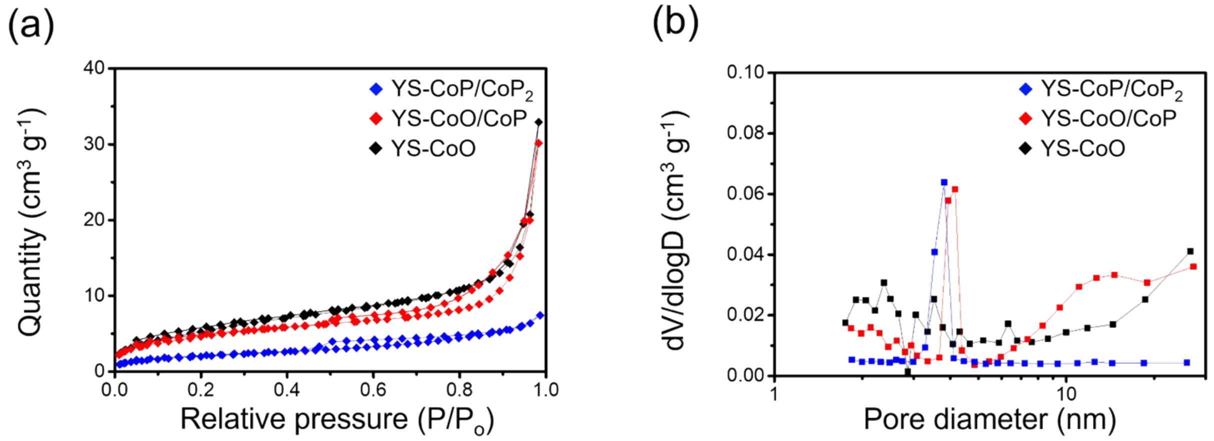

Figure S4. (a) Brunauer-Emmett-Teller (BET) and (b) Barrett-Joyner-Halenda (BJH) of YS-CoO, YS-CoO/CoP and YS-CoP/CoP_2.

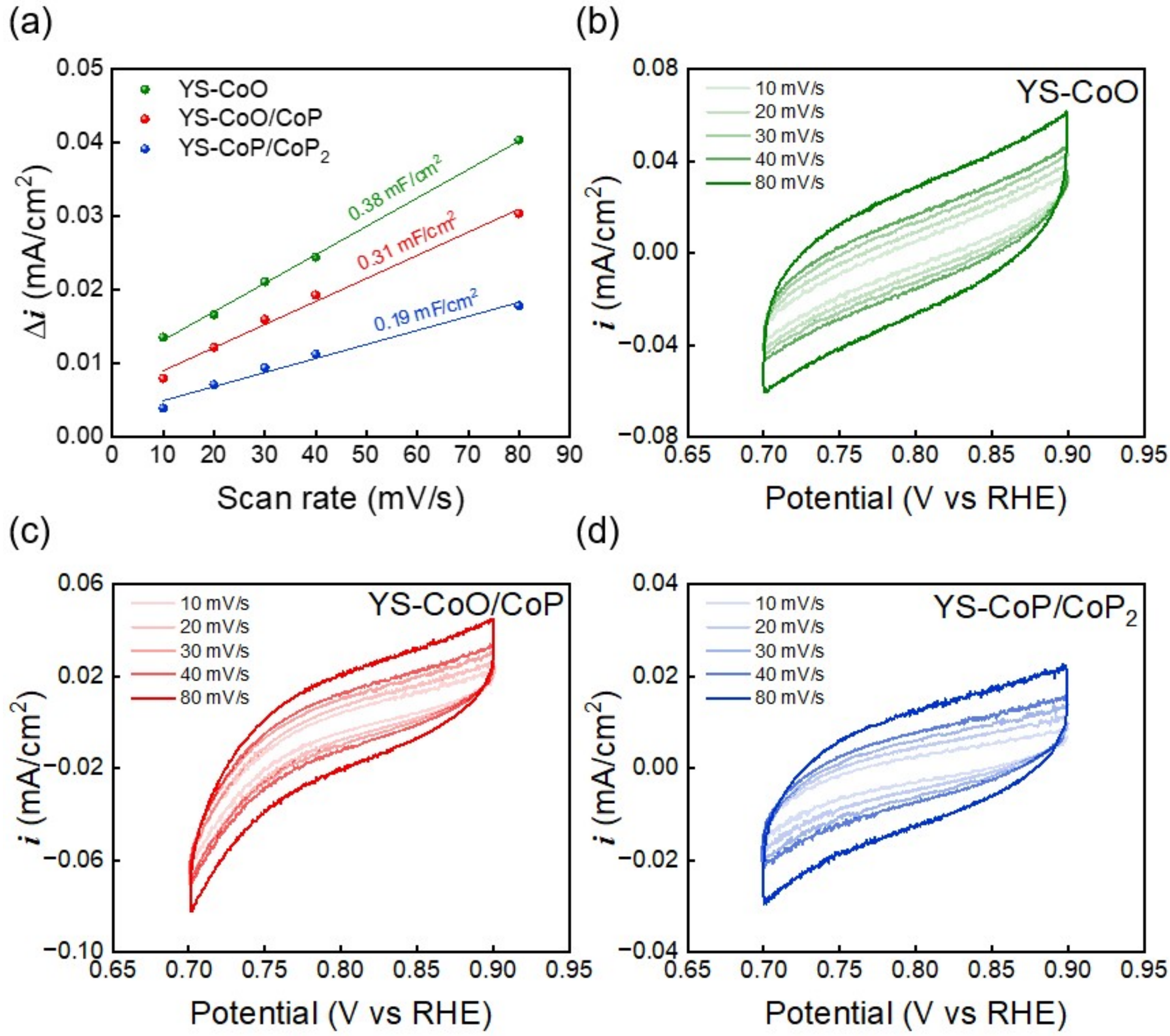

Figure S5. (a) Double layer capcitance and cyclic voltametry of (b) YS-CoO, (c) YS-CoO/CoP and (d) YS-CoP/CoP_2 in different scan rate.

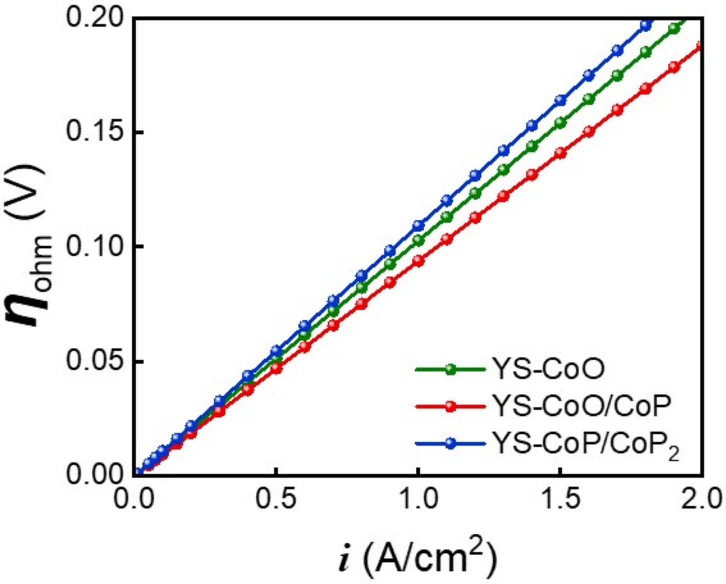

Figure S6. The ohmic loss of AEM electrolyzers equipped with YS-CoO, YS-CoO/CoP and YS-CoP/CoP_2.

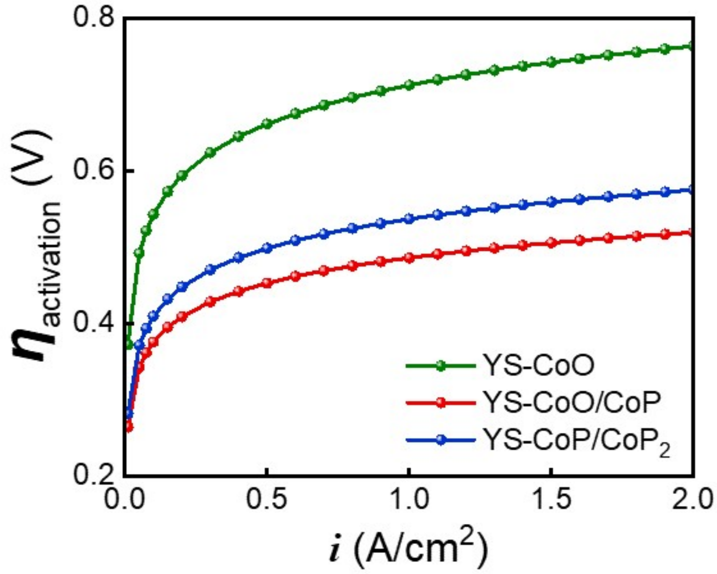

Figure S7. The activation loss of AEM electrolyzers equipped with YS-CoO, YS-CoO/CoP and YS-CoP/CoP_2.

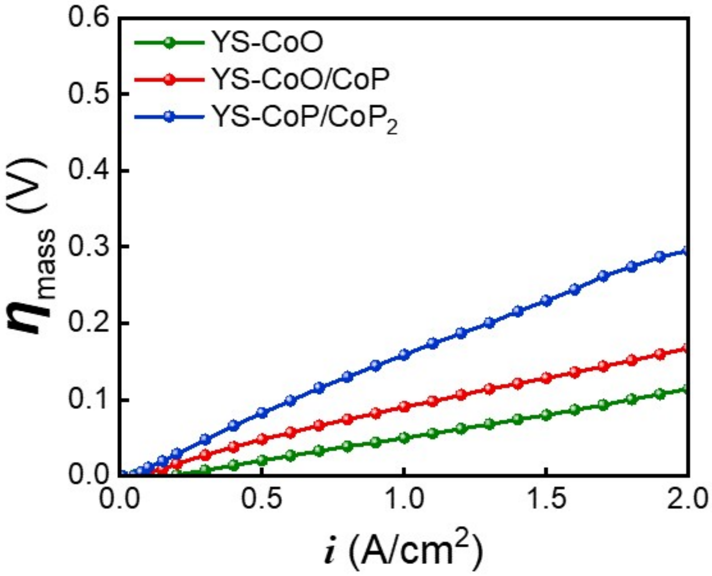

Figure S8. The mass transport loss of AEM electrolyzers equipped with YS-CoO, YS-CoO/CoP and YS-CoP/CoP_2.

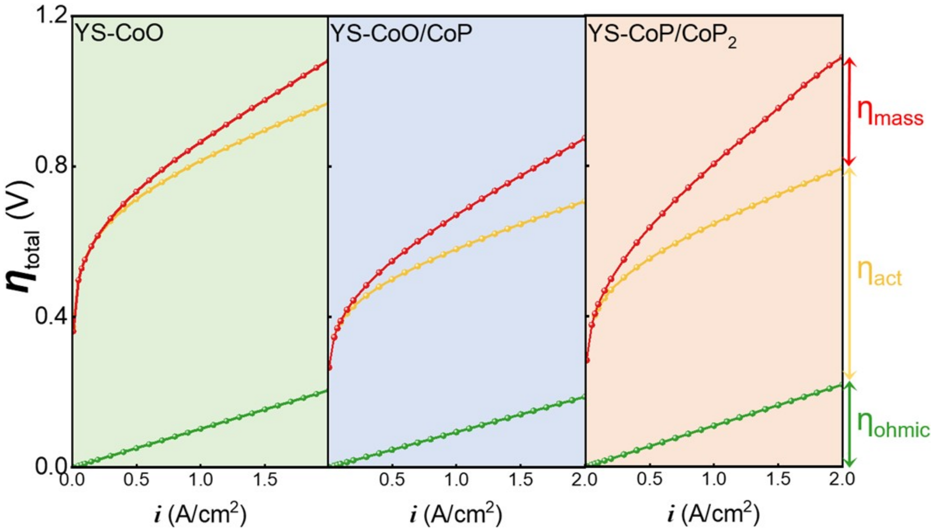

Figure S9. The total voltage loss of AEM electrolyzer equipped with YS-CoO, YS-CoO/CoP and YS-CoP/CoP_2.

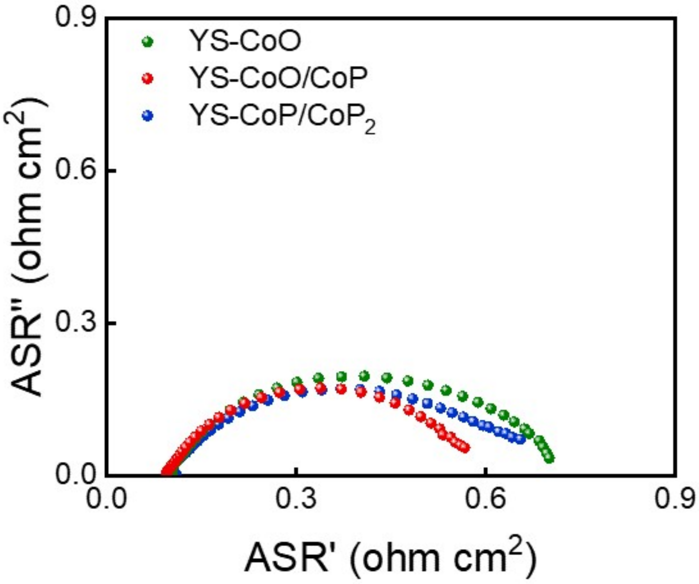

Figure S10. The nyquist plots of AEM electrolyzers equipped with YS-CoO, YS-CoO/CoP and YS-CoP/CoP_2 at 0.1 A cm^{-2}.

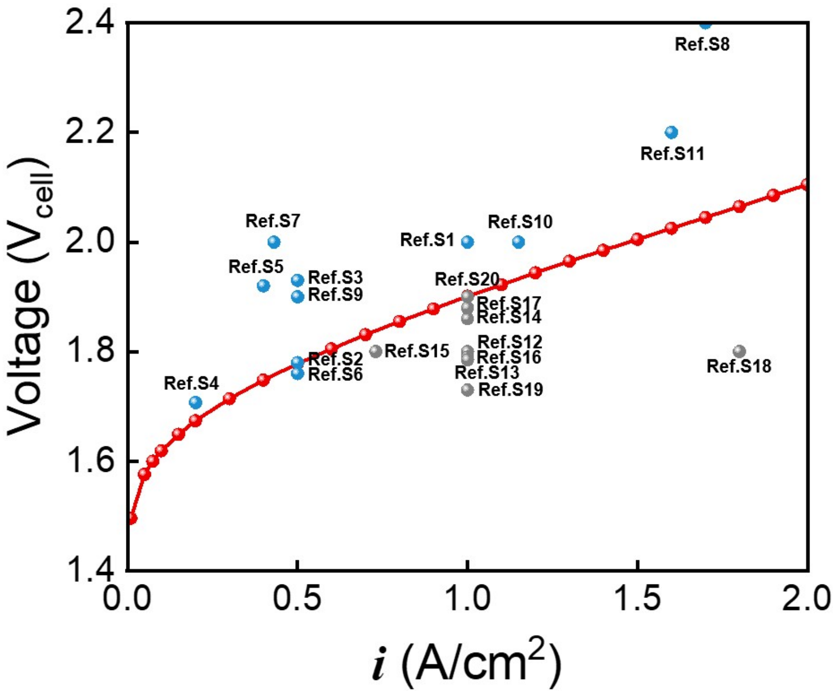

Figure S11. Performance of AEM electrolyzer equipped with YS-CoO/CoP in comparison to previous studies.

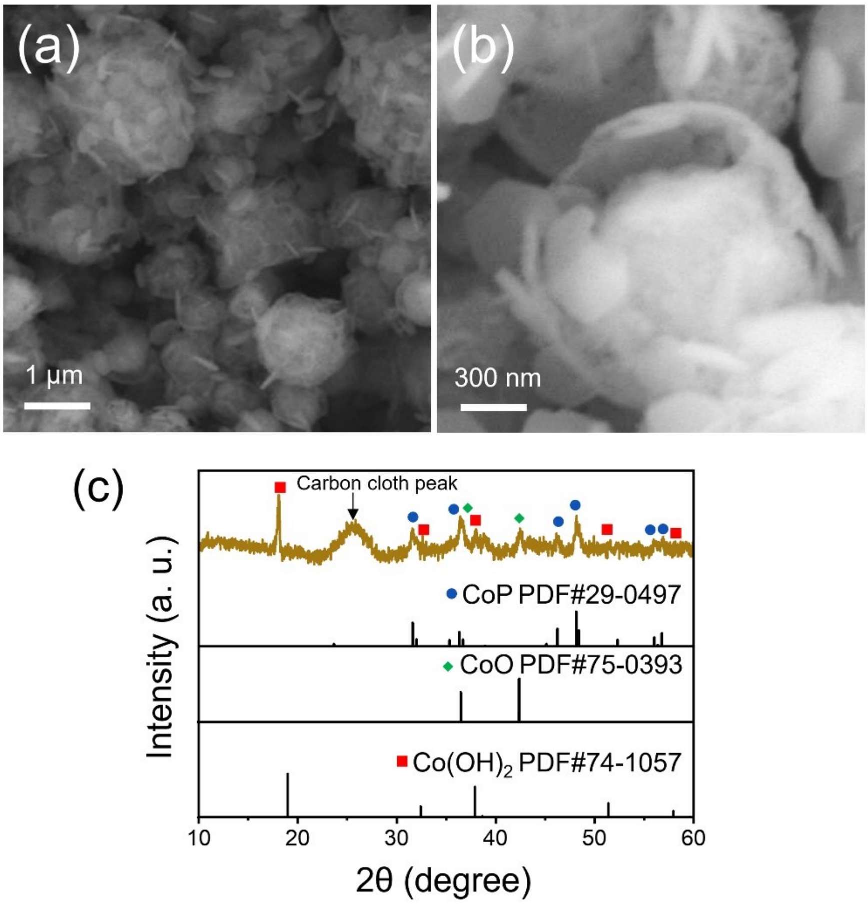

Figure S12. (a-b) SEM images of after durability test YS-CoO/CoP (c) XRD patterns of after durability test YS-CoO/CoP

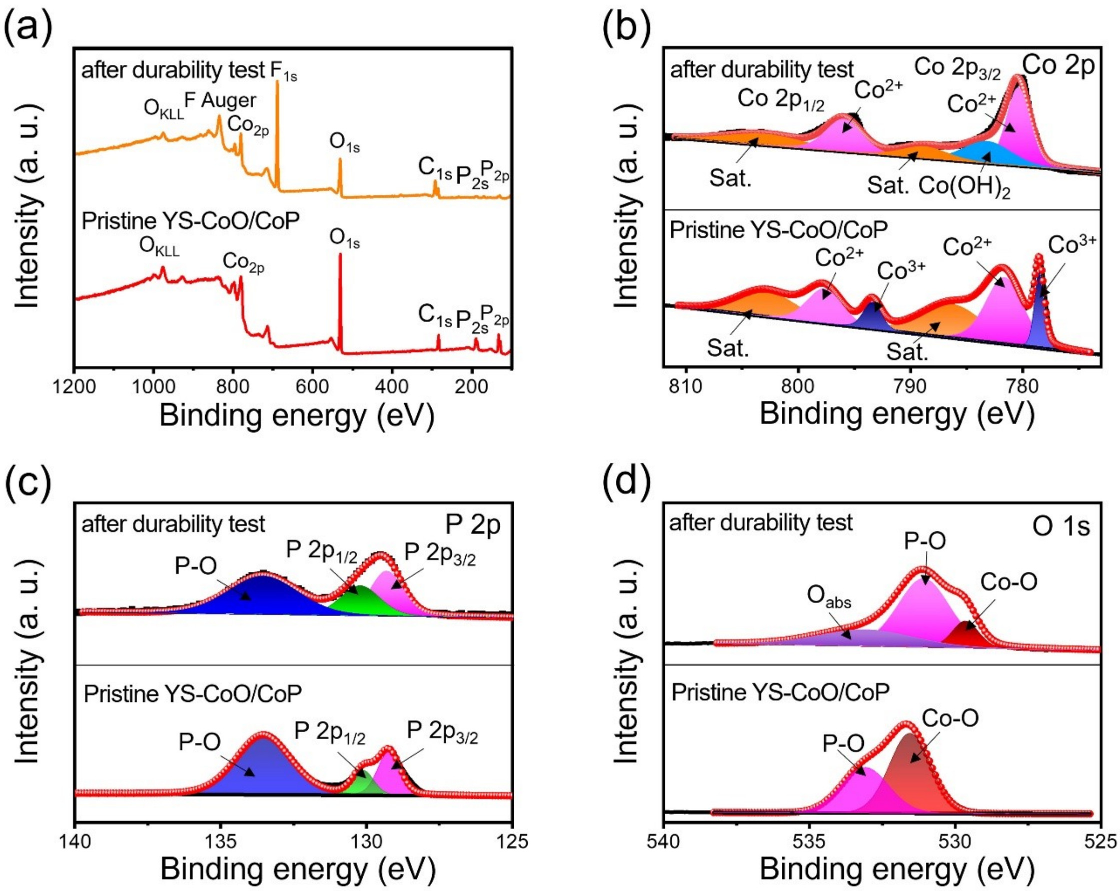

Figure S13. Chemical states of pristine YS-CoO/CoP and after stability test YS-CoO/CoP. (a) Survey spectra of pristine YS-CoO/CoP and after stability test YS-CoO/CoP. high-resolution XPS spectra of pristine YS-CoO/CoP and after stability test YS-CoO/CoP (b) Co 2p, (c) P 2p, and (d) O 1s.

sample	Molar ratio (%)	
	Co	P
YS-CoO	79.74	20.26
YS-CoO/CoP	49.36	50.64
YS-CoP/CoP_2	42.48	57.52

Table S1. Molar ratio of YS-CoO, YS-CoO/CoP and YS-CoP/CoP_2 analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES).

Table S2. Comparison of the performance of AEM electrolyzer with previous studies.

Cathode catalyst	Anode catalyst	Testing conditions	Activity	Ref.
YS-CoO/CoP	NiFe LDH	1 M KOH at 55 °C	0.6 A cm^{-2} at 1.8 V	This work
a-Ni@Ni(OH)$_2$/Ti	IrO_2/CP	1 M KOH at 50 °C	1.0 A cm^{-2} at 2.0 V	S1
NiFe LDH	Pt-AC/Cr-N-C	1 M KOH at 80 °C	0.5 A cm^{-2} at 1.78 V	S2
NiCoP$_v$@NF	NiCoP$_v$@NF	1 M KOH	0.5 A cm^{-2} at 1.93 V	S3
NiFe LDH	NiFe LHD-PMo12	1 M KOH at 60 °C	0.2 A cm^{-2} at 1.707 V	S4
NiS	NiFe LDH/NiS	30 % KOH at 85 °C	0.4 A cm^{-2} at 1.92 V	S5
CoN/VN@NF	P-CoVO@NF	1 M KOH at 70 °C	0.5 A cm^{-2} at 1.76 V	S6
Co_3S_4 NS/NF	$Cu_{0.81}Co_{2.19}O_4$ NS/NF	1 M KOH at 45 °C	431 mA cm^{-2} at 2.0 V	S7
Ni-Co-S/CP	IrO_x/CP	1 M KOH at 50 °C	1.7 A cm^{-2} at 2.4 V	S8
NiMoCo	NiFeCr-LDH	1 M KOH at 40 °C	0.5 A cm^{-2} at 1.9 V	S9
Ni-MoO_2	$Ni_{0.6}Co_{0.2}Fe_{0.2}$	1 M KOH at 50 °C	1.15 A cm^{-2} at 2.0 V	S10
Ni-Fe-Co	Ni-Fe-O_x	1 M KOH at 60 °C	1.6 A cm^{-2} at 2.2 V	S11
Pt(OH)(O_3)/Co(P)	Pt(OH)(O_3)/Co(P)	0.1 M KOH at 80 °C	1.0 A cm^{-2} at 1.8 V	S12
NiRu/C (10 wt% Ru)	NiFe-LDH	1 M KOH at 70 °C	1.0 A cm^{-2} at 1.73 V	S13
RuP_2	IrO_2	1 M KOH at 50 °C	1.0 A cm^{-2} at 1.86 V	S14

PtNi	Co	1 M KOH at 80 °C	0.73 A cm^{-2} at 1.8 V	S15
Ru SAs/WC_x	$NiFeOH_x$/ NF	1 M KOH at 80 °C	1 A cm^{-2} at 1.79 V	S16
Pt-Ru/RuO_2	NiFe-LDH	0.1 M KOH at 60 °C	1 A cm^{-2} at 1.9 V	S17
Ru-NiCr LDH-r	NiFe LDH/NF	1 M KOH at 80 °C	1.8 A cm^{-2} at 1.8 V	S18
Ru/CoSA/CNT	$NiFeOH_x$/ NF	1 M KOH at 80 °C	1 A cm^{-2} at 1.785 V	S19
Ru/C_{60}-300	IrO_2	1 M KOH at 60 °C	1 A cm^{-2} at 1.88 V	S20

Table S3. Comparison of yolk-shell structure materials reported in the previous literatures.

Application	Morphology	Material	Synthesis method	Ref.
HER	Spherical	RuP_2-C@RuP_2-C	Template assistance	S21
HER	Spherical	Mn-Co-P	Hydrothermal & post treatment	S22
HER	Spherical	Mn–Co_2P	self-templated hydrothermal	S23
HER	Spherical	Rh/N S	self-template synthesis	S24
HER	Spherical	C−MoS_2	Sub-Nanoreactor	S25
HER, ORR, OER	Spherical	Co-CoO	Heat-pyrolysis	S26
HER, OER	Spherical	NiS_2/MoS_2	Hydrolysis & post treatment	S27
DSSCs, HER	polyhedral	NC-CoS_2@CoS_2/MoS_2	Anion exchange & annealing	S28
OER	polyhedral	$(Co_{1-x}Ni_x)_3O_4$	Hard template	S29
OER	polyhedral	ZnSe@ $CoSe_2$	Template assistance	S30

References

[S1] W. Guo, J. Kim, H. Kim, S. Hong, H. Kim, S. Y. Kim and S. H. Ahn, Materials Today Chemistry, 2022, 24, 100994.

[S2] L. Zeng, Z. Zhao, Q. Huang, C. Zhou, W. Chen, K. Wang, M. Li, F. Lin, H. Luo, Y. Gu, L. Li, S. Zhang, F. Lv, G. Lu, M. Luo and S. Guo, Journal of the American Chemical Society, 2023, 145, 21432-21441.

[S3] L. Guo, J. Chi, T. Cui, J. Zhu, Y. Xia, H. Guo, J. Lai and L. Wang, Advanced Energy Materials, 2024, 14, 2400975.

[S4] Z. Cai, P. Wang, J. Zhang, A. Chen, J. Zhang, Y. Yan and X. Wang, Advanced Materials, 2022, 34, 2110696.

[S5] Q. Wen, K. Yang, D. Huang, G. Cheng, X. Ai, Y. Liu, J. Fang, H. Li, L. Yu and T. Zhai, Advanced Energy Materials, 2021, 11, 2102353.
[S6] Z. Liang, D. Shen, Y. Wei, F. Sun, Y. Xie, L. Wang and H. Fu, Advanced Materials, 2024, 36, 2408634.
[S7] Y. S. Park, J. H. Lee, M. J. Jang, J. Jeong, S. M. Park, W.-S. Choi, Y. Kim, J. Yang and S. M. Choi, International Journal of Hydrogen Energy, 2020, 45, 36-45.
[S8] W. Guo, J. Kim, H. Kim and S. H. Ahn, International Journal of Energy Research, 2021, 45, 1918-1931.
[S9] M. H. Wang, Z. X. Lou, X. Wu, Y. Liu, J. Y. Zhao, K. Z. Sun, W. X. Li, J. Chen, H. Y. Yuan, M. Zhu, S. Dai, P. F. Liu and H. G. Yang, Small, 2022, 18, 2200303.
[S10] A. Y. Faid, A. O. Barnett, F. Seland and S. Sunde, ACS Appl Energy Mater, 2021, 4, 3327-3340.
[S11] I. Vincent, E.-C. Lee and H.-M. Kim, RSC Advances, 2020, 10, 37429-37438.
[S12] L. Zeng, Z. Zhao, F. Lv, Z. Xia, S.-Y. Lu, J. Li, K. Sun, K. Wang, Y. Sun, Q. Huang, Y. Chen, Q. Zhang, L. Gu, G. Lu and S. Guo, Nature Communications, 2022, 13, 3822.
[S13] S. Ruck, A. Hutzler, S. Thiele and C. van Pham, Small Methods, 2024, DOI: 10.1002/smtd.202401179, e2401179.
[S14] J.-C. Kim, J. Kim, J. C. Park, S. H. Ahn and D.-W. Kim, Chemical Engineering Journal, 2021, 420, 130491.
[S15] S. M. Alia, M. A. Ha, C. Ngo, G. C. Anderson, S. Ghoshal and S. Pylypenko, ACS Catal, 2020, 10, 9953-9966.
[S16] X. Lin, W. Hu, J. Xu, X. Liu, W. Jiang, X. Ma, D. He, Z. Wang, W. Li, L. M. Yang, H. Zhou and Y. Wu, J Am Chem Soc, 2024, 146, 4883-4891.
[S17] Y. Zhu, M. Klingenhof, C. Gao, T. Koketsu, G. Weiser, Y. Pi, S. Liu, L. Sui, J. Hou, J. Li, H. Jiang, L. Xu, W.-H. Huang, C.-W. Pao, M. Yang, Z. Hu, P. Strasser and J. Ma, Nature Communications, 2024, 15, 1447.
[S18] J. Yang, S. Yang, L. An, J. Zhu, J. Xiao, X. Zhao and D. Wang, ACS Catalysis, 2024, 14, 3466-3474.
[S19] D. Wang, W. Liu, H. Wang, S. Lu, Y. Li, S. Guo and Y. Xiang, Advanced Functional Materials, n/a, 2417976.
[S20] W. Yang, Q. Huang, Y. Yan, Y. Li, T. Xu, A. Yu, Y. Zhao, P. Peng, Y. Wang, L. Echegoyen and F.-F. Li, Angewandte Chemie International Edition, n/a, e202414149.
[S21] J. Luo, J. Wang, Y. Guo, J. Zhu, H. Jin, Z. Zhang, D. Zhang, Y. Niu, S. Hou and J. Du, *Appl. Catal., B*, 2022, 305, 121043

[S22] G. Tang, Y. Zeng, B. Wei, H. Liang, J. Wu, P. Yao and Z. Wang, *Energy Technol*, 2019, 7, 1900066.
[S23] Z. Zhang, S. Chen, S. Chen, Z. Yuan, Y. Fang, D. Dang and Y. Zheng, *Int. J. Hydrogen. Energy*, 2022, 47, 32493-32502.
[S24] X. Bu, Y. Bu, Q. Quan, S. Yang, Y. Meng, D. Chen, Z. Lai, P. Xie, D. Yin and D. Li, *Adv. Funct. Mater.*, 2022, 32, 2206006.
[S25] F. Gong, Y. Liu, Y. Zhao, W. Liu, G. Zeng, G. Wang, Y. Zhang, L. Gong and J. Liu, *Angew. Chem.*, 2023, 135, e202308091.
[S26] M. Yang, D. Wu and D. Cheng, *Int. J. Hydrogen. Energy*, 2019, 44, 6525-6534.
[S27] Q. Zhang, B. Liu, Y. Ji, L. Chen, L. Zhang, L. Li and C. Wang, *Nanoscale*, 2020, 12, 2578-2586.
[S28] J. Yang, C. Zhang, Y. Niu, J. Huang, X. Qian and K.-Y. Wong, *Chem. Eng. J.*, 2021, 409, 128293.
[S29] H. Wang, D. Zhang, H. Sun, Q. Wang, Z. Li, J. Qi and B. Wang, *Appl. Surf. Sci.*, 2023, 613, 156088.
[S30] Y. Xing, S. Zhao, J. Wu, X. Tang, Y. Zhang, Z. Zou, K. Huang and X. Xiong, *J. Alloy. Compd.*, 2023, 947, 169501.