Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
This journal is © The Royal Society of Chemistry 2022

Engineering the Surface Anatomy of an Industrially Durable $NiCo_2S_4/NiMo_2S_4/NiO$ Bifunctional electrode for Alkaline Seawater Electrolysis

*Selvaraj Seenivasan, and Do-Heyoung Kim**

School of Chemical Engineering, Chonnam National University, 300 Youngbong-dong, Gwangju 500-757, Republic of Korea

SUPPORTING INFORMATION

*Corresponding author: kdhh@chonnam.ac.kr

Tel. (office): +82-62-530-1894

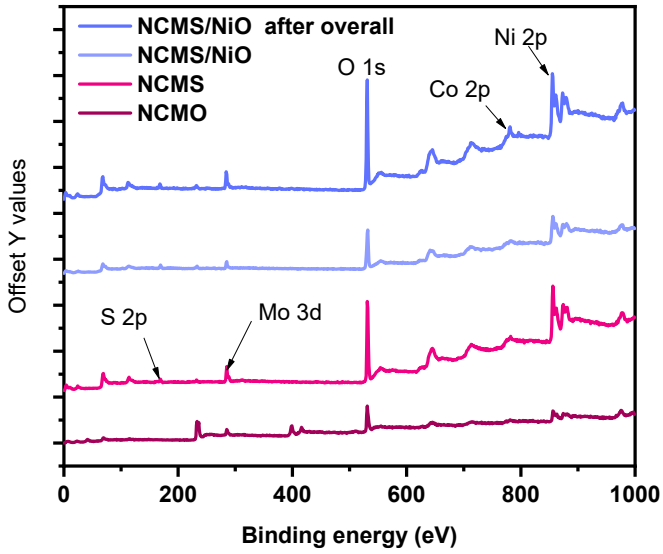


Fig. S1. XPS survey spectra of bare ($NiCo_2O_4$/$NiMoO_4$) NCMO, ($NiCo_2S_4$/$NiMo_2S_4$) NCMS, ($NiCo_2S_4$/$NiMo_2S_4$/NiO) NCMS/NiO (before and after overall water splitting for 14 days) electrocatalysts.

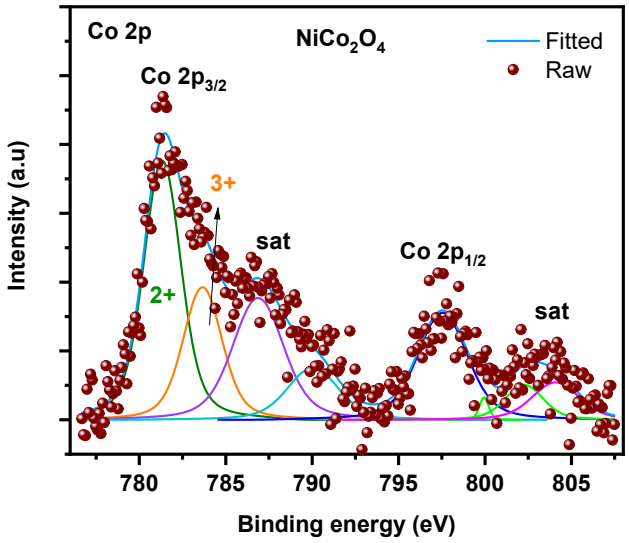


Fig. S2. High resolution Co 2p spectra of $NiCo_2O_4$ sample. There are two main peaks in Co $2p_{3/2}$ at 783.69 and 781.27 eV, which can be assigned to the 3+ and 2+ states of $NiCo_2O_4$, respectively.

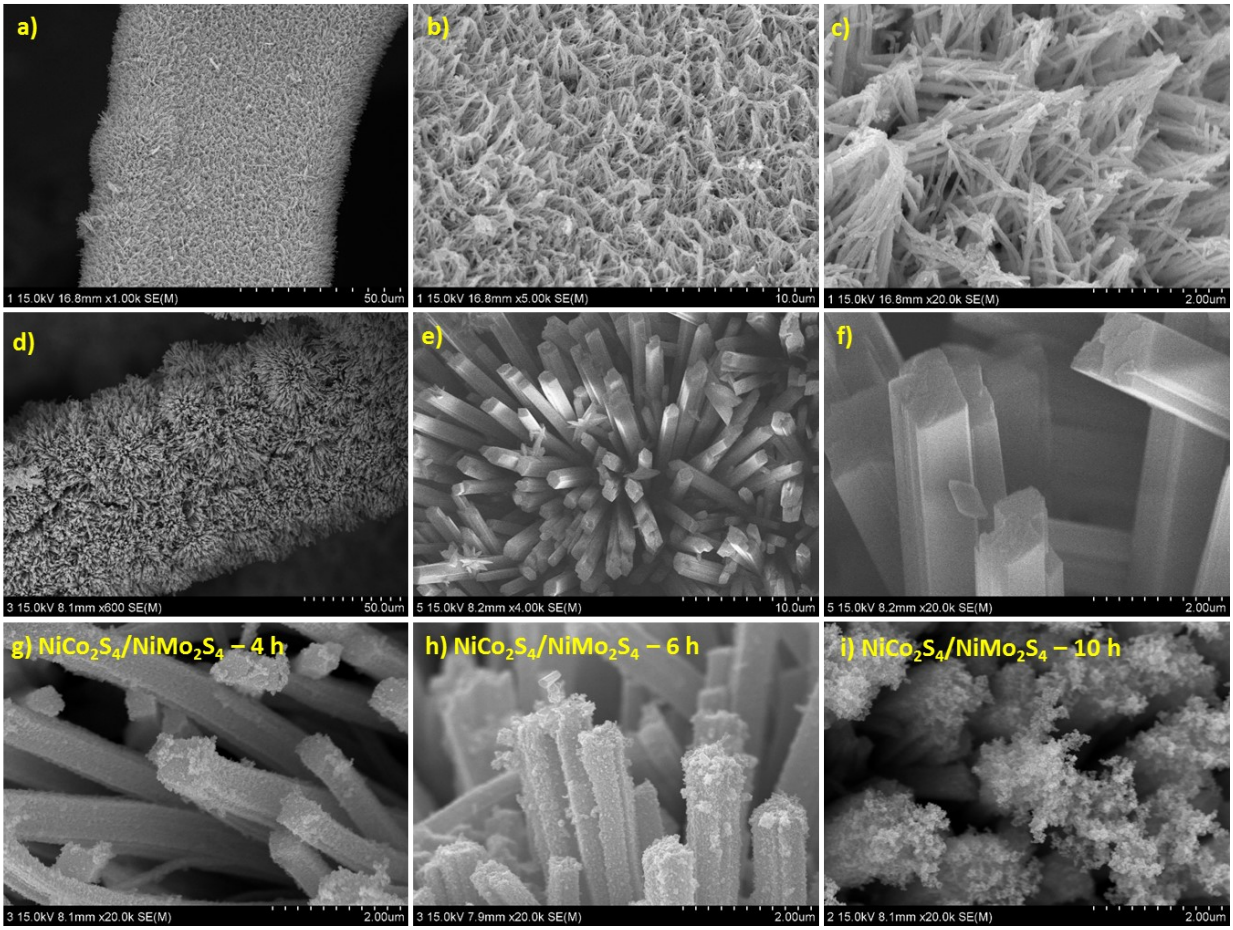


Fig. S3. HR-SEM images of $NiCo_2O_4$ (a-c), $NiCo_2O_4/NiMoO_4$ (d-f) and $NiCo_2S_4/NiMo_2S_4$ derived with three different anion exchange reaction duration (g-i)

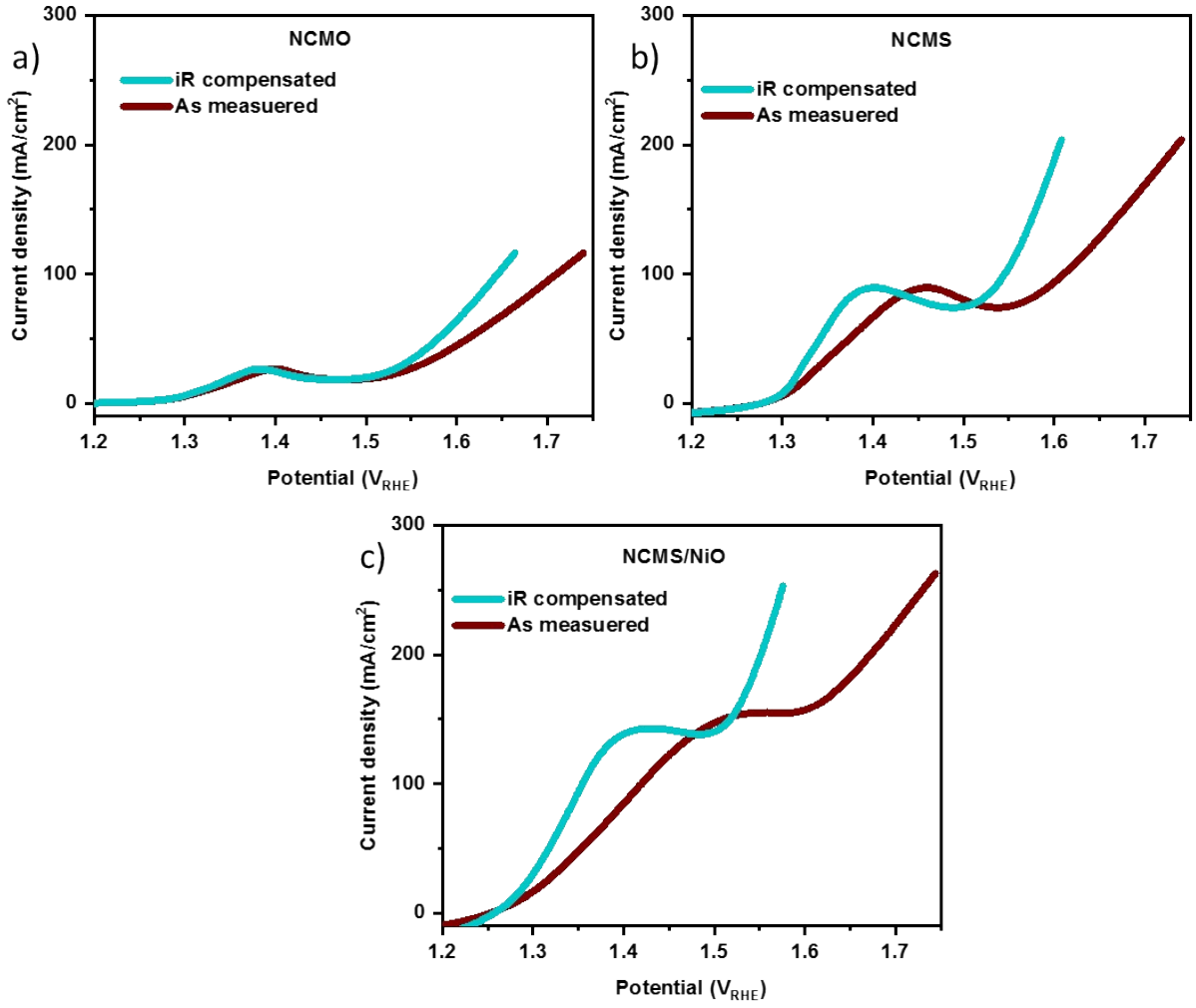


Fig. S4. (a-c) OER half-cell forward sweep LSV curves with and without iR compensation.

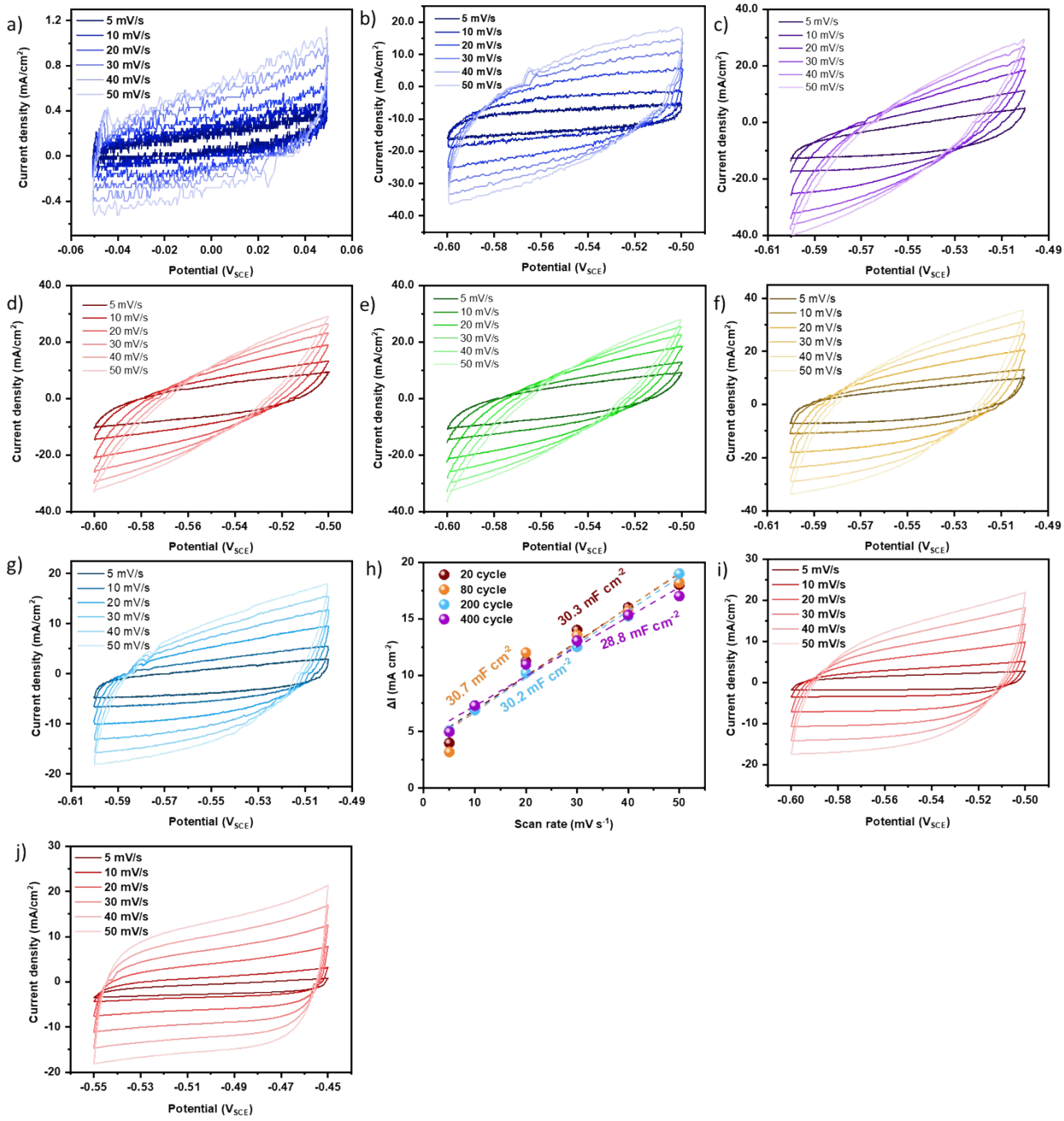


Fig. S5. CV measurements at scan rate of 5, 10, 20, 30, 40 and 50 mV/s in 1 M KOH. a) NCMO, b) NCMS, and NCMS/NiO with various number NiO ALD cycles c) 20, d) 40, e) 80, f) 200 and g) 400. h) Estimation of double-layer capacitance (C_{dl}) by plotting the variation in current density ($\Delta I = (I_a - I_c)/2$) versus the scan rate. CV measurements at scan rate of 5, 10, 20, 30, 40 and 50 mV/s in 1 M KOH. i) used NCMS/NiO OER electrode and j) used NCMS/NiO HER electrode.

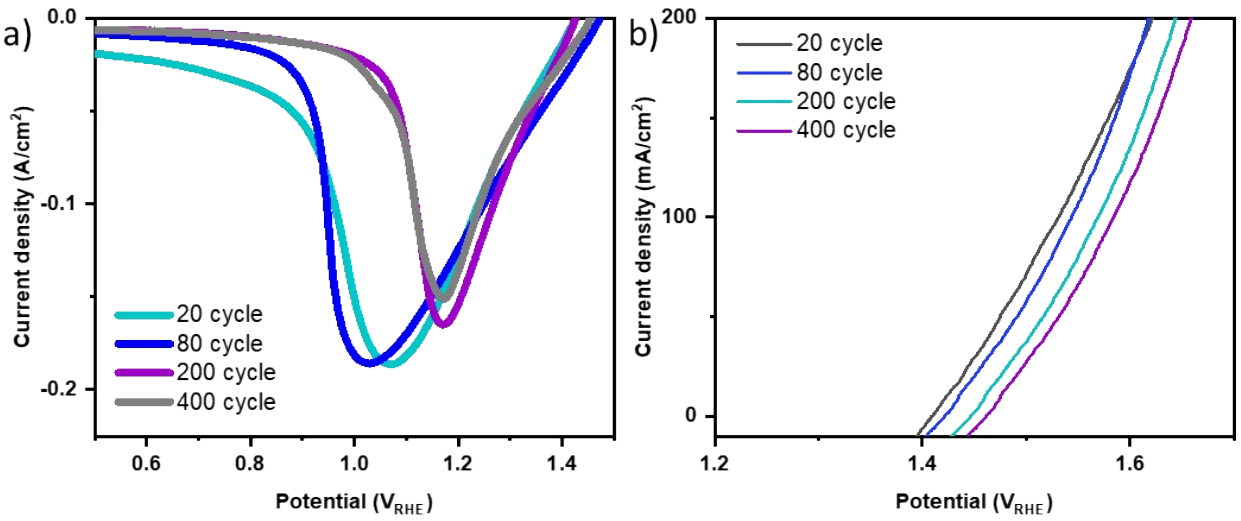


Fig. S6. a) Reduction peak (from CV curves) of NCMS/NiO at 100 mV/s scan rate with various number of NiO ALD cycles (20, 80, 200 and 400), and b) corresponding reverse sweep LSV curves (iR compensated).

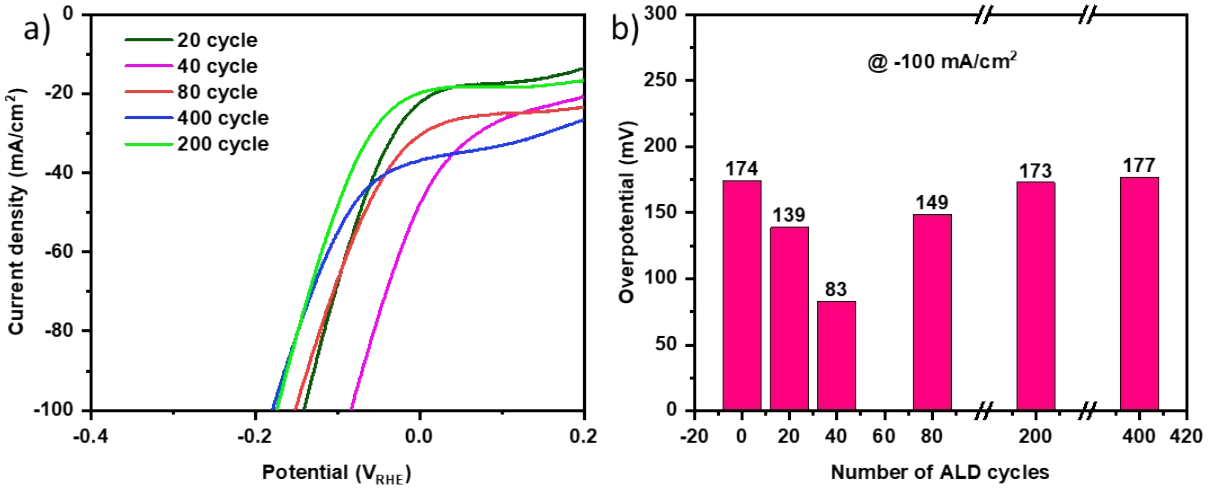


Fig. S7. a) LSV (iR compensated) curves in HER half-cell with respect to number of ALD cycles, b) corresponding overpotential required for -100 mA/cm^2.

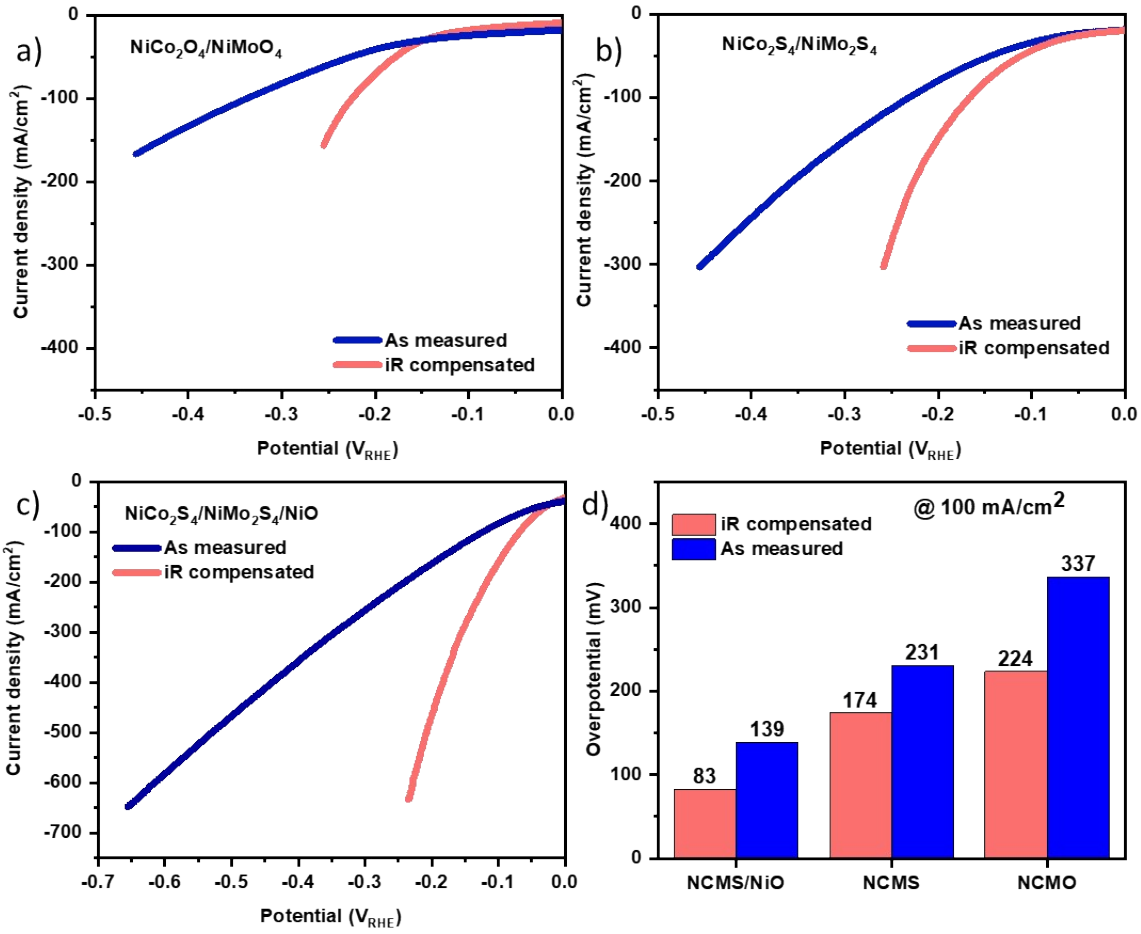


Fig. S8. HER half-cell LSV curves with and without iR compensation (a-c) and the overpotential comparison of all three catalysts at -100 mA/cm^2 current density in 1 M KOH electrolyte.

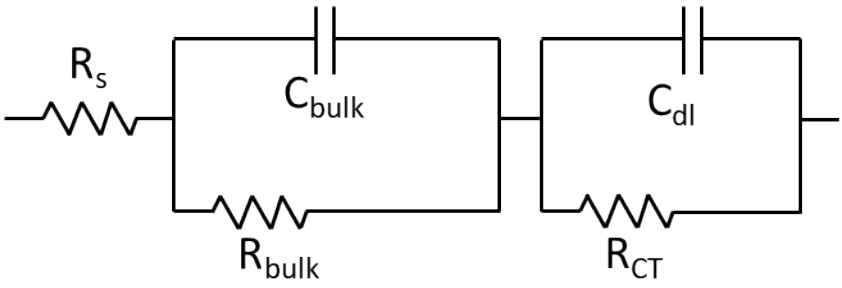


Fig. S9. Electronic circuit used to fit the impedance data.

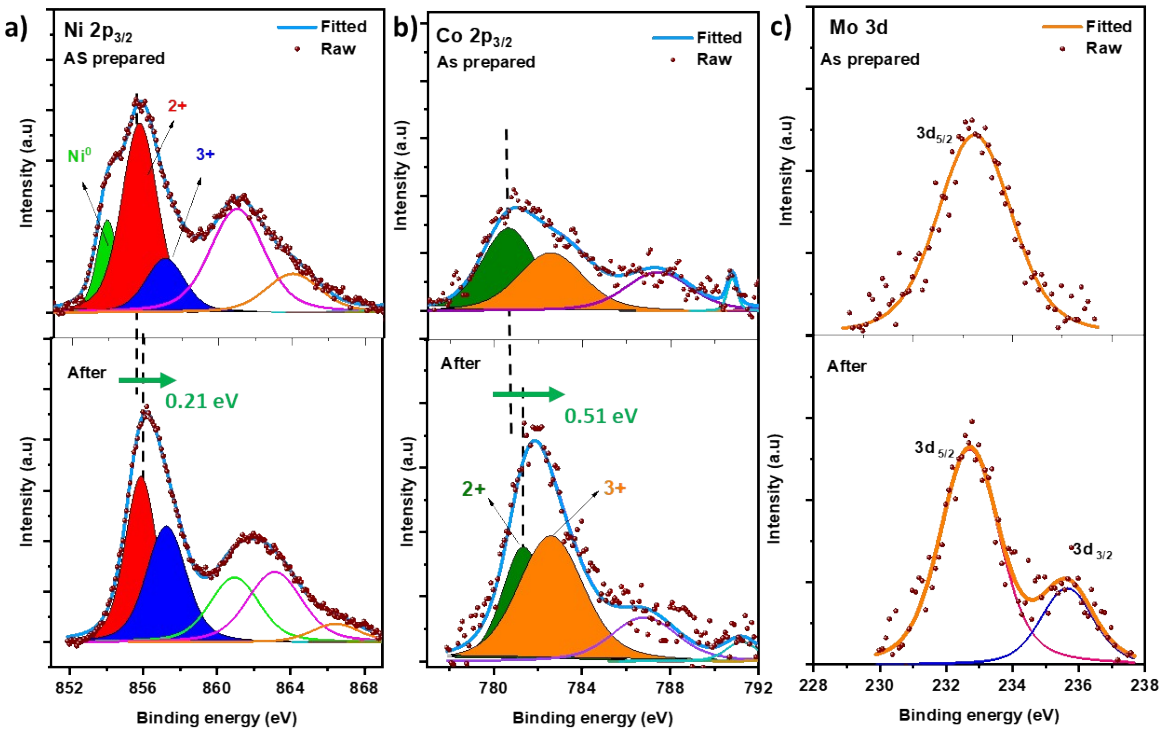


Fig. S10. Comparison of high-resolution XPS profile for a) Ni $2p_{3/2}$, b) Co $2p_{3/2}$, and c) Mo 3d of NCMS/NiO before and after 7 consecutive LSV curves (anodic sweep from 1.0 V_{RHE} to 1.8 V_{RHE}, 5 mV s^{-1}).

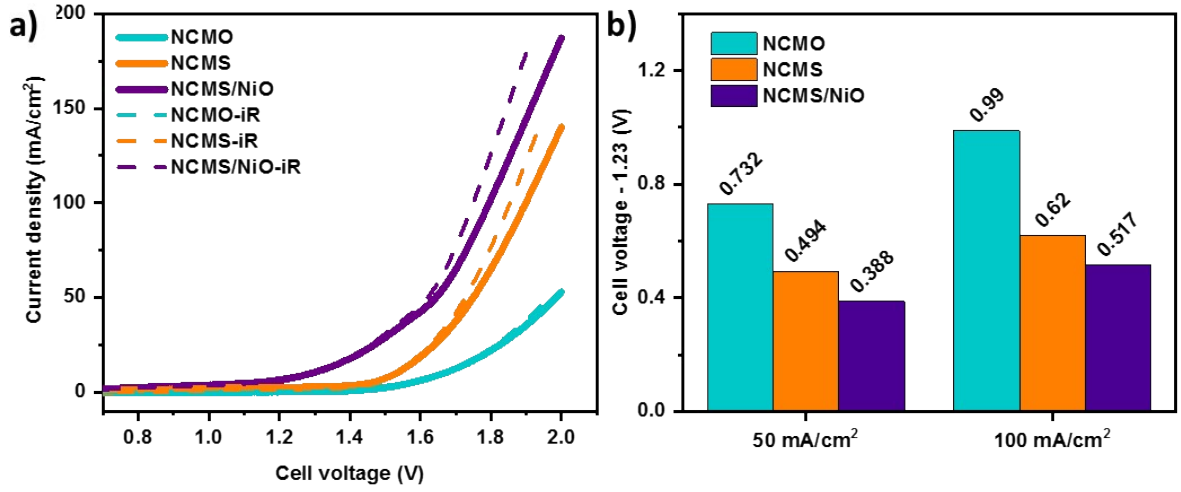


Fig. S11. a) LSV curves of NCMO, NCMS, and NCMS/NiO electrocatalysts in two electrode cell, for overall water splitting in 1 M KOH electrolyte. b) Comparison of overpotential required

(additional to the thermodynamic requirement of 1.23 V) to deliver 50 and 100 mA/cm^2 current densities with iR compensation.

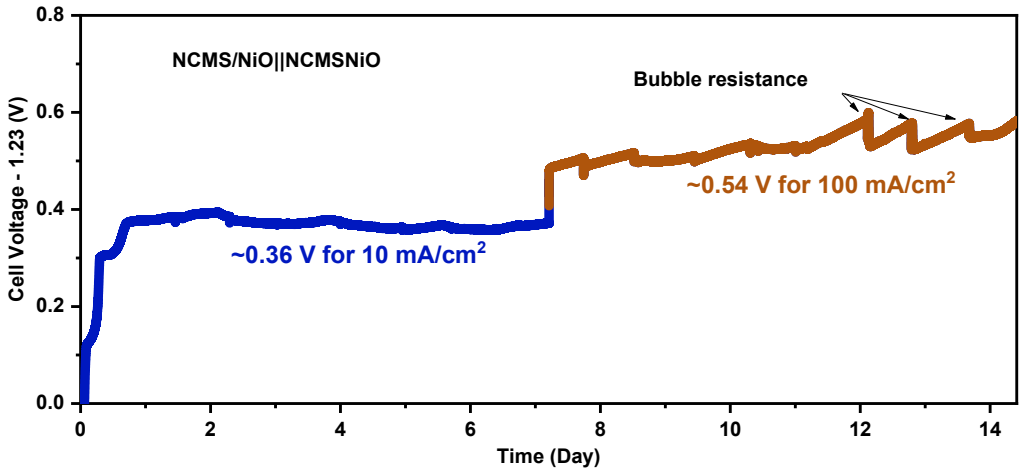


Fig. S12. Chronopotentiometry of NCMS/NiO catalysts in the overall water splitting (1 M KOH + DI water) for 14 days (1-7 days at 10 mA/cm^2 and 8-14 days at 100 mA/cm^2).

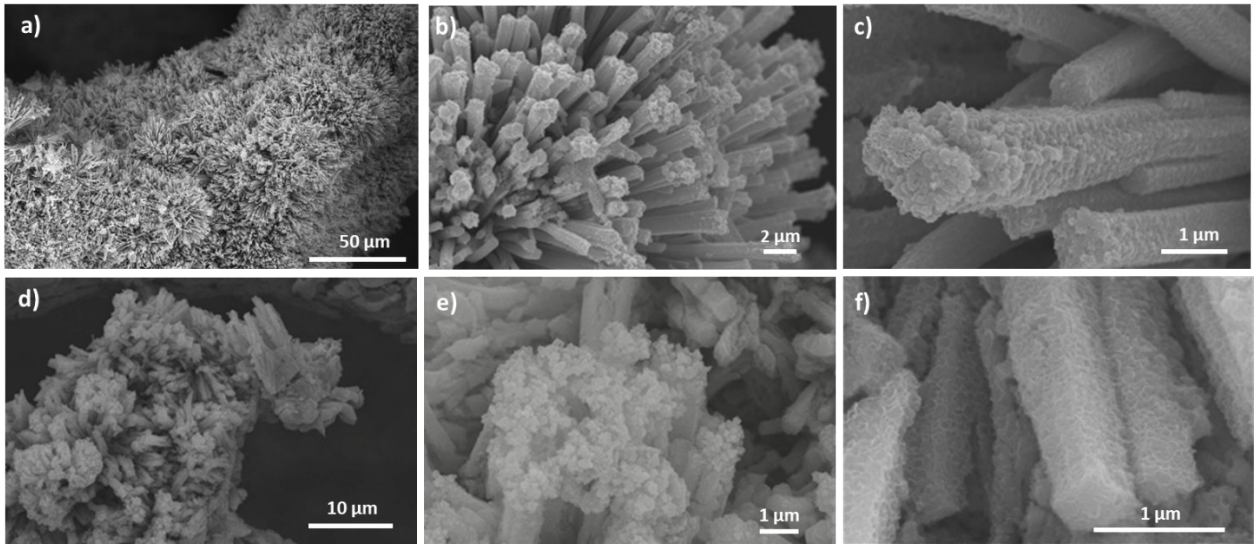


Fig. S13. The HR-SEM images of NCMS/NiO electrocatalyst after overall water splitting for 14 days (first week at 10 mA/cm^2 and second week at 100 mA/cm^2): a-c) OER electrode and d-f) HER electrode.

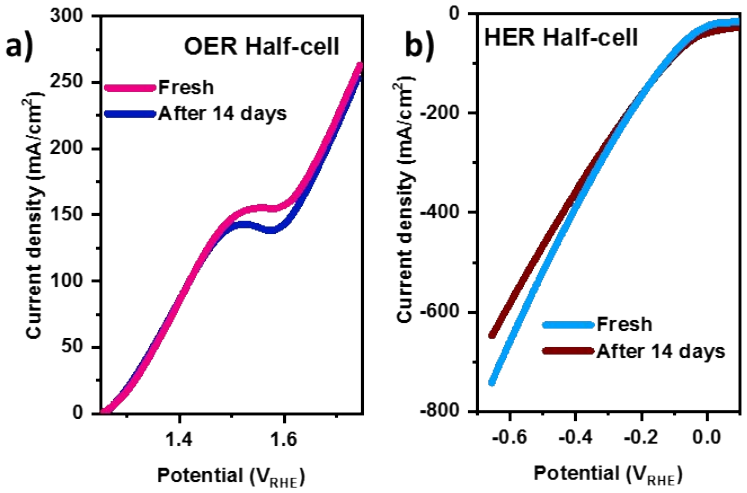


Fig. S14. Comparison LSV curves (iR uncompensated) of NCMS/NiO catalysts before and after the CA test: a) OER half-cell, b) HER half-cell.

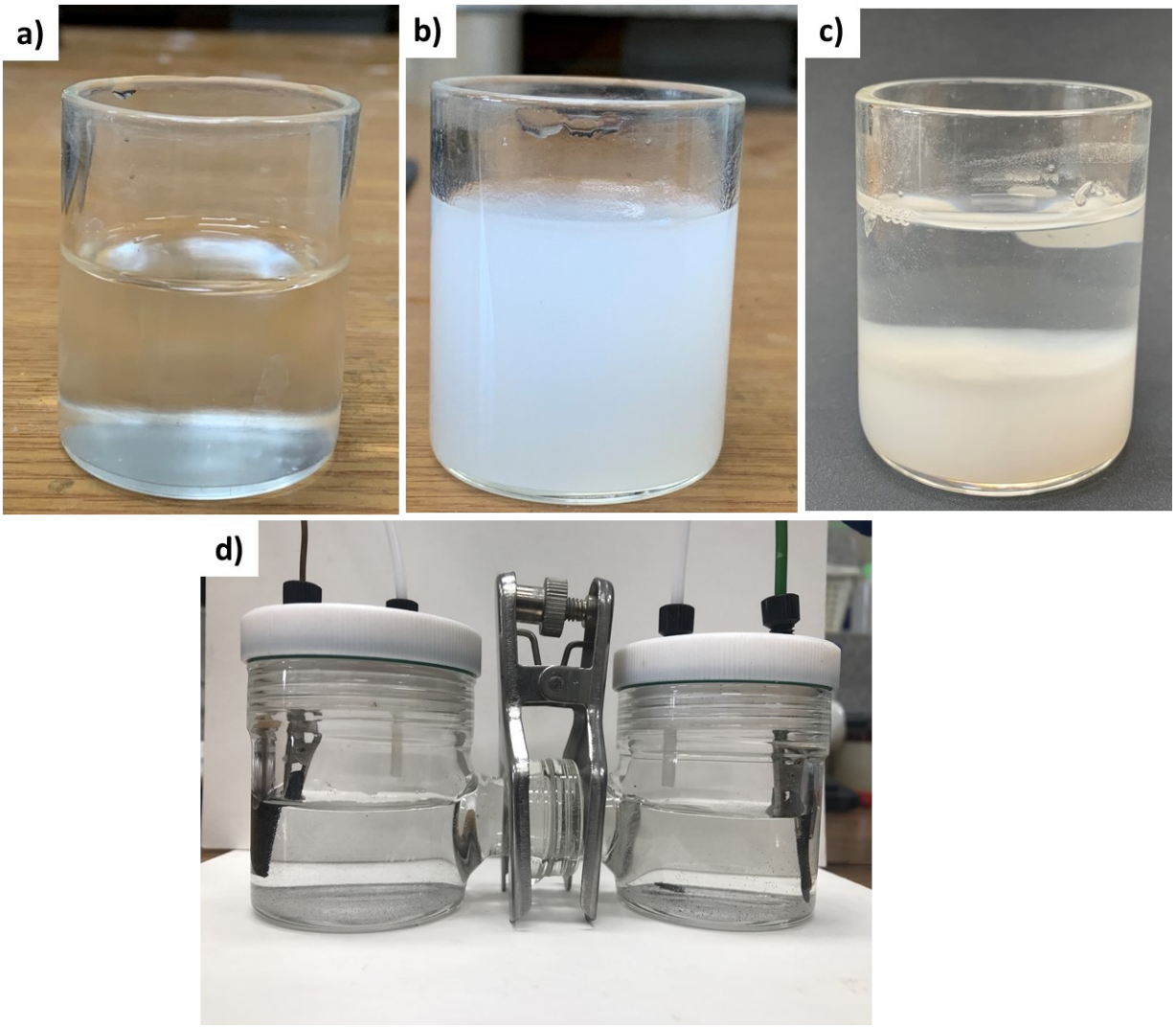
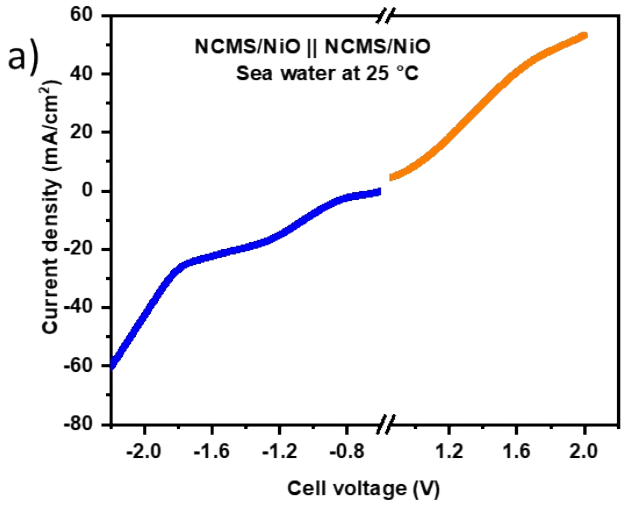
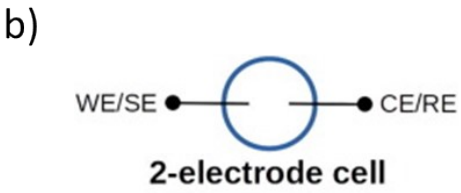
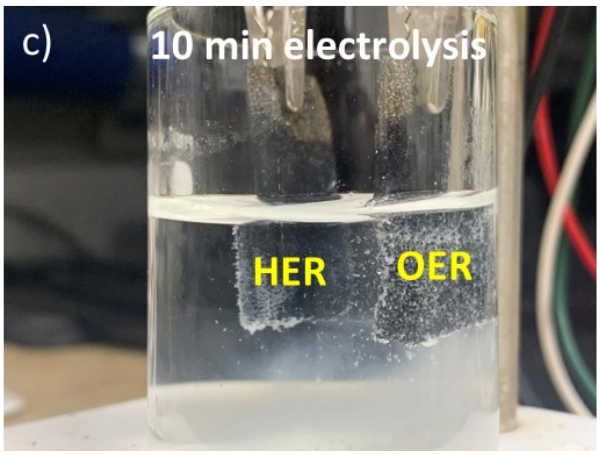


Fig. S15. Digital photographs of a) raw sea water after simple filtration to remove debris and fine sand particles, b) 1 M KOH in sea water, and c) insoluble $Mg(OH)_2$/$Ca(OH)_2$ and $CaCO_3$ particles settled at the bottom of the beaker after an hour. d) Digital image of industrial seawater electrolyzer cell at 80 °C.





	WE/SE	CE/RE
Orange curve	Anode	Cathode
Blue curve	Cathode	Anode



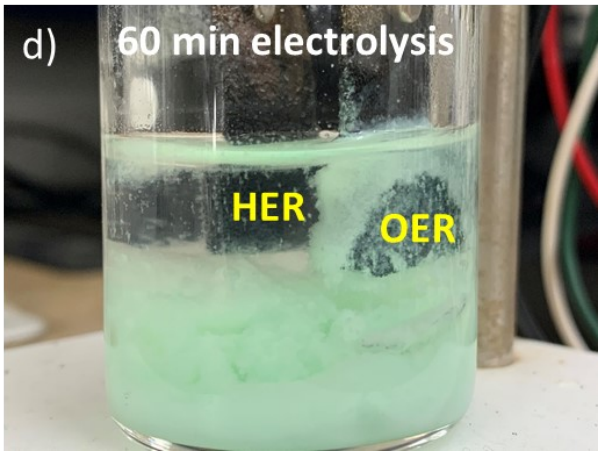


Fig. S16. a) LSV of NCMS/NiO || NCMS/NiO overall water splitting cell in raw sea water electrolyzer (pH ~ 8.1). Orange and blue curve indicated the current density measured at the anode and cathode, respectively. b) Cell configuration used to obtain the orange and blue LSV curves. WE is working, SE is working sense, CE is counter and RE is reference electrode connecting terminals of the potentiostat. c) Digital image of electrolyzer after 10 min of continuous electrolysis at 50 mA/cm^2 current density. The formation of insoluble particles over electrodes can be seen. After 60 min (d) the anode severely covered by the insoluble particles.

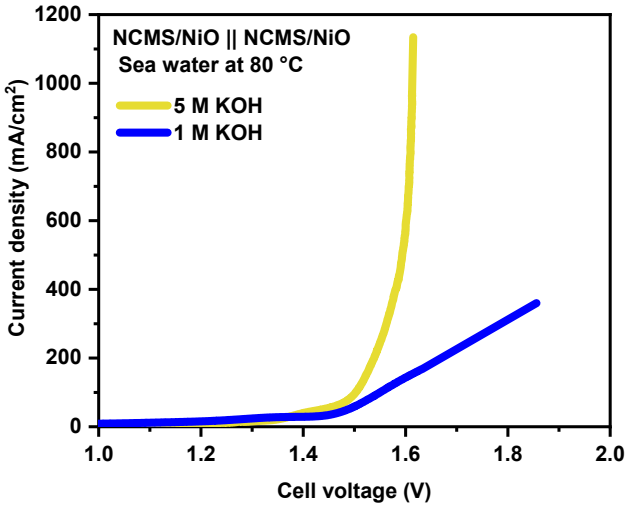


Fig. S17. Linear sweep voltammetry of NCMS/NiO || NCMS/NiO overall water splitting cell in industrial sea water electrolyzer with iR compensation.

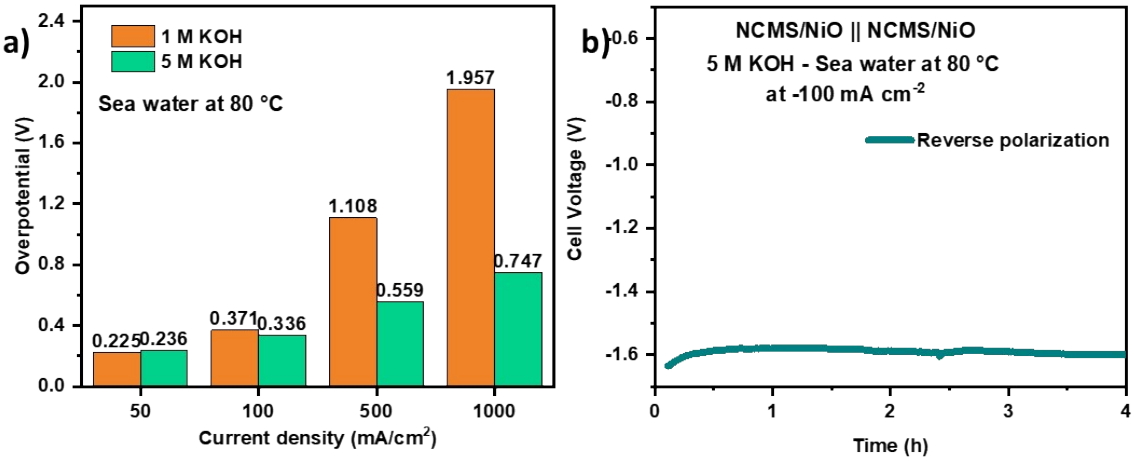


Fig. S18. a) Comparison of total overpotentials achieved by NCMS/NiO||NCMS/NiO electrolyzer under reverse polarization. b) Chronopotentiometric response recorded by using reversely polarized NCMS/NiO electrodes at -100 mA/cm^2 for 4 h.

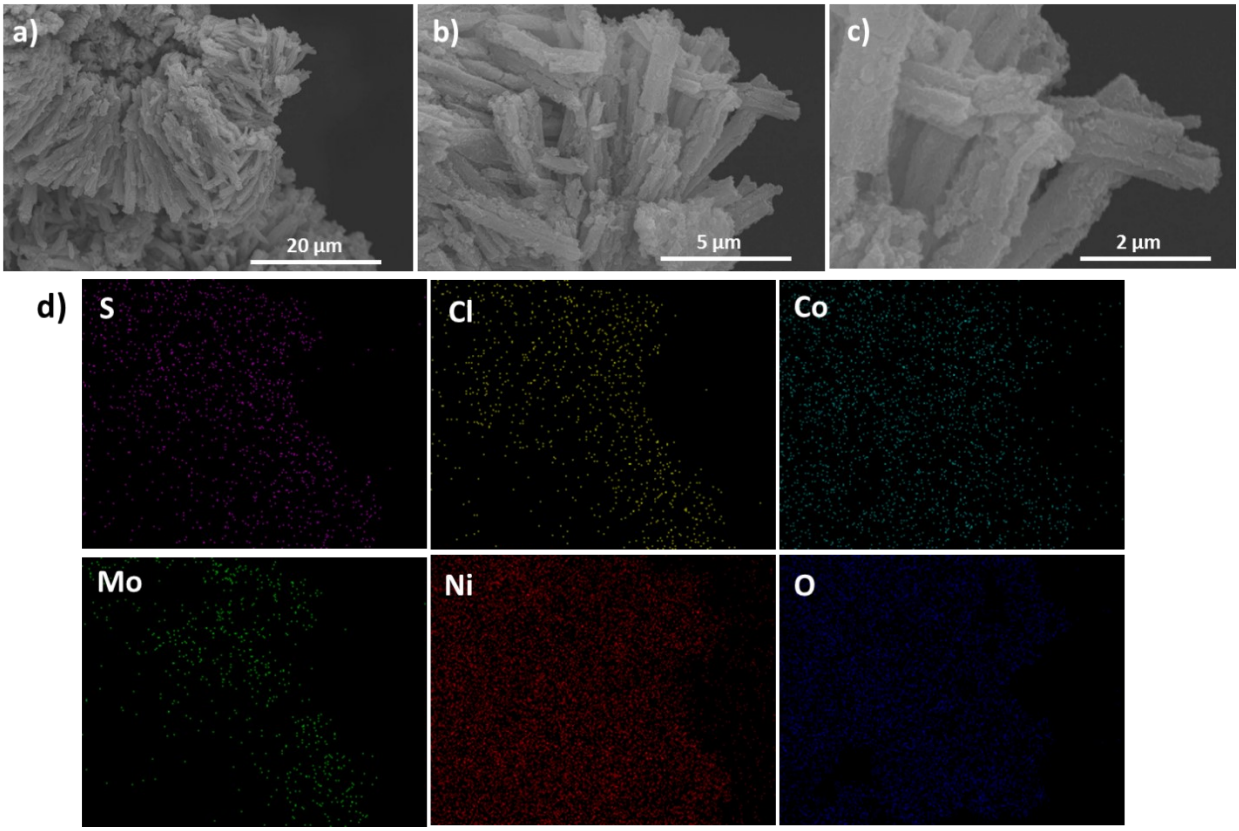


Fig. S19. The HR-SEM images (a-c) of HER electrode after industrial water splitting for 30 days and corresponding elemental analysis (d).

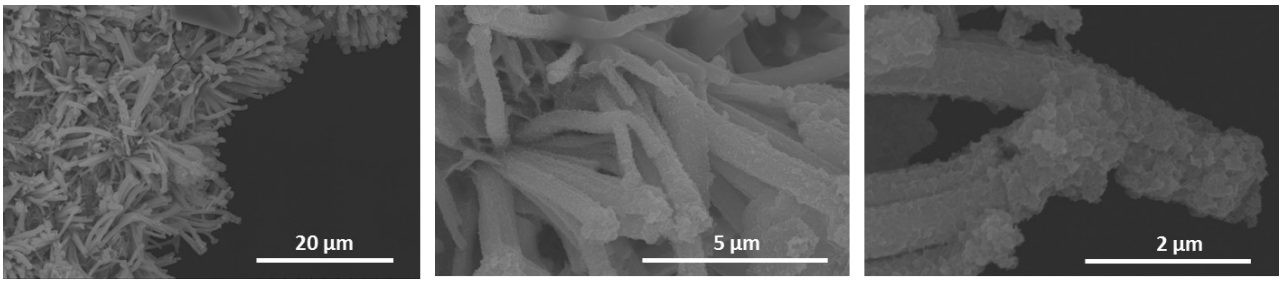


Fig. S20. a-c) The HR-SEM images of OER electrode after overall seawater splitting at 10 mA/cm^2 current density and 25 °C.

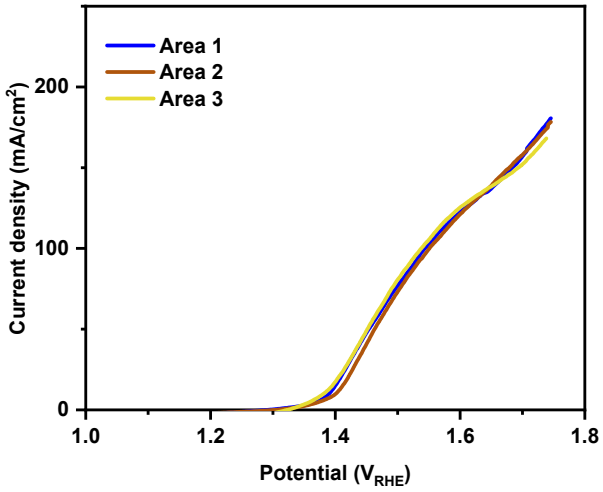


Fig. S21. LSV curves (without iR compensation) of the areas mentioned in Fig. 10(a) in the manuscript for the OER half-cell (1 M KOH + DI water, at 25 °C).

Table S1. Atomic percentage of each element from XPS measurements.

Electrocatalyst	Ni	Co	Mo	O	S
NCO	10.6	21.8	-	67.6	-
NCMO	13.8	0.0	13.8	70.5	-
NCMS	23.0	2.8	1.0	65.6	7.6
NCMS/NiO	23.7	0.9	0.8	67.7	7.0

Table S2. The calculated double layer capacitance (C_{dl}) and ECSA from CV measurements of NCMO, NCMS, and NCMS/NiO-X (X= number of ALD cycles) in 1 M KOH.

Electrocatalyst	C_{dl} (mF cm^{-2})	ECSA (cm^2)
NCMO	3.1	77
NCMS	26.9	672

NCMS/NiO-20	30.3	757
NCMS/NiO-40	30.8	770
NCMS/NiO-80	30.7	767
NCMS/NiO-200	30.2	755
NCMS/NiO-400	28.8	720

Table S3. Summary of recent reports on OER and HER half-cell performance in 1 M KOH electrolyte with fresh water/deionized water**.** All overpotentials for 10 mA/cm^2 current density except specially mentioned.

S.No	Catalyst	HER overpotential (mV)	OER overpotential (mV)	Stability (h)	Ref
1	$NiCo_2S_4$/$NiMo_2S_4$/ ALD-NiO	20	186	336	This work
		83 for 100 mA/cm^2	263 for 100 mA/cm^2		
2	$NiCo_2S_4$/NiS	203 for 100 mA/cm^2	264 for 100 mA/cm^2	240	[1]
3	NiMoN	38	290 for 50 mA/cm^2	50	[2]
4	NiMoN	22	230	36	[3]
5	NiMoN/Ni_3N	28	-	24	[4]
6	NiMoN/Ni_3N	37	277	20	[5]
7	Ni_3FeN/r-GO	94	270	100	[6]
8	$Fe_{0.9}Ni_{2.1}S_2$	72	252 for 100 mA/cm^2	100	[7]

9	Fe-NiMoN	264 for 100 mA/cm^2	305 for 100 mA/cm^2	24	[8]
10	Mo_2C/Mo_2N	-	276 for 50 mA/cm^2	40	[9]
11	NiFe-MS/MOF	90	243 for 100 mA/cm^2	27	[10]
12	Ni_7S_6	70	140	24	[11]
13	P-Fe_3N	102	270	60	[12]
14	F doped CoS_2	112	366	100	[13]
15	NiCoN	68	247	24	[14]
16	Co_4N-CeO_2/Graphite	24	239	50	[15]
17	W_2N/WC	148.5	320	10	[16]
18	CoVFeN	-	281 for 100 mA/cm^2	100	[17]
19	$CuNi_2N$	71.4	312 for 100 mA/cm^2	60	[18]
20	Co-Mo_5N_6	280 for 1000 mA/cm^2	-	10	[19]
21	P-$NiCo_2O_4$/NF	55	300	10	[20]
22	$Ni_5P_4/NiCo_2O_4$/NF	27	-	48	[21]
23	N-Doped $NiCo_2O_4$@C	42	242	24	[22]
24	N-$NiMoO_4/NiS_2$	99	283	20	[23]
25	$NiCo_2S_4$	80	243	24	[24]
26	Mo-Ni_3S_2/Ni_xP_y	109	238 at 50 mA/cm^2	48	[25]

	IrO_2	-	287 at 50 mA/cm^2	-	
	Pt/C	37	-	-	
27	CDs/$NiCo_2S_4$/Ni_3S_2	116	127	12	[26]
28	lily like $CoNi_2S_4$	54	328 at 100 mA/cm^2	10	[27]
29	P-$NiCo_2S_4$	74	-	-	[28]
30	$NiCo_2O_4$/$NiMoS_4$	159	310 at 20 mA/cm^2	12	[29]
31	$CuCo_2S_4$ NW	65	310 at 100 mA/cm^2	20	[30]
32	Ni-Co-P	107	270	20	[31]
33	NiFe LDH@Ni_3N/NF	108 for 100 mA/cm^2	238 for 100 mA/cm^2	100	[32]
34	$NiCo_2S_4$@g-C_3N_4-CNT	330	-	-	[33]
35	CoP/NiCoP	210 for 100 mA/cm^2	-	24	[34]
	Pt/C	205 for 100 mA/cm^2	-	-	
36	NiMoN/NiFeN	84 for 100 mA/cm^2	277 for 100 mA/cm^2	48	[35]
	NiMoN	56 for 100 mA/cm^2	350 for 100 mA/cm^2	48	
37	SS wire/Ni_4Mo	63 for 100 mA/cm^2	-	156	[36]
	SS wire/Ni-FeOOH	-	257 for 100 mA/cm^2	48	

Table S4. Fitted data of electrochemical impedance spectra data shown in Fig. 4(i) and 5(e).

	Catalyst	R_S (Ω)	C_{bulk} (mF)	R_{bulk} (Ω)	C_{dl} (mF)	R_{CT} (Ω)
HER	**NCMO**	1.210	0.001	0.245	0.342	0.972
	NCMS	1.032	0.058	0.162	0.254	0.378
	NCMS/NiO	1.036	0.078	0.165	0.248	0.249
OER	**NCMO**	0.796	0.024	0.142	0.642	1.642
	NCMS	0.789	0.044	0.027	0.744	0.569
	NCMS/NiO	0.787	0.037	0.018	0.616	0.331

Table S5. Comparison of overpotential required for 100 mA/cm^2 current density (extracted from LSV curves) in a two electrode cell with different electrolyte concentration and temperature.

Catalyst	Electrolyte	Without iR compensation (mV)	With iR compensation (mV)
NCMO	1 M KOH + DI water	1040	990
NCMS	1 M KOH + DI water	665	620
NCMS/NiO	1 M KOH + DI water	561	517
	1 M KOH + Sea water	527	453
	1 M KOH + Sea water at 80 °C	377	305
	5 M KOH + Sea water at 80 °C	252	252
	5 M KOH + Sea water at 80 °C After 30 days	275	275

Table S6. Elemental analysis through SEM-EDS measurements of used NCMS/NiO anode (OER) samples in two electrode cell chronopotentiometry experiments.

Element	As prepared (At %)	After 14 days in DI water electrolysis (At %)	After 30 days in high temperature sea water electrolysis (At %)
O	22.37	24.18	35.02
Mo	1.97	0.96	1.26
S	32.43	26.50	18.09
Co	2.77	5.29	6.11
Ni	40.46	43.07	39.51

Table S7. Performance comparison between NCMS/NiO||NCMS/NiO cell and other reported non-noble metal based electrolyzers in different alkaline simulated and natural seawater. Natural seawater contains approximately 3.5 % NaCl concentration. The overpotentials are mentioned without iR compensation.

S.No	Electrode OER || HER	Electrolyte	Current density (mA/cm^2)	Overpotential (mV)	Stability (h)	Ref
1	$NiCo_2S_4/NiMo_2S_4$/ ALD-NiO || $NiCo_2S_4/NiMo_2S_4$/ ALD-NiO	1 M KOH + Seawater	100	527	100	This work
		1 M KOH + Seawater at 80 °C		377	100	
		5 M KOH + Seawater at 80 °C		252	720	

			500	524	100	
2	$NiFe/NiS_x$ || NiO/Cr_2O_3	1 M KOH + 1.5 M NaCl	400	790	1000	[37]
		1 M KOH + Seawater	400	890	1000	
		6 M KOH + 1.5 M NaCl at 80 °C	400	490	1000	
3	NiMoN/NiFeN || NiMoN	1 M KOH + Seawater	100	395	-	[35]
			500	751	-	
		6 M KOH + Seawater	100	270	600	
4	NiFe LDH || Pt	0.1 M KOH + 0.5 M NaCl	10	359	2	[38]
5	$Co_2[Fe(CN)_6]$ || NiMoS	Phosphate buffer + Seawater (pH~7)	10	870	20	[39]
6	CoSe || CoSe	Natural Seawater (pH~7)	10	570	-	[40]
7	Ni_3N/Ni_3S_2 || Ni_3N/Ni_3S_2	Natural Seawater (pH~7)	48.3	570	-	[41]
8	S-(Ni/Fe)OOH || $NiCoN/Ni_xP$	Natural Seawater (pH~7)	10	580	24	[42]
9	FeOOH/NiCoOOH/ Graphene oxide	1 M KOH + 0.5 M NaCl at 60 °C	1000	770	378	[43]
10	$NiCo_2S_4/NiS$ || $NiCo_2S_4/NiS$	6 M KOH + Seawater at 80	100	337	240	[1]

		°C	1000	743	-	

Table S8. Atomic percentage of each element from XPS measurements of used OER and HER NCMS/NiO electrode after industrial electrolysis for 30 days.

	S 2p	Ni 2p	O 2p	Cl 2p	Ca 2p	Mg 2p
OER	3.24	24.14	36.13	2.86	0.0	0.0
HER	1.93	22.44	37.25	0.19	1.44	0.0

References:

1. S. Seenivasan, H. Jung, J. W. Han and D.-H. Kim, *Small Methods*, 2022, **6**, 2101308.
2. B. Chang, J. Yang, Y. L. Shao, L. Zhang, W. L. Fan, B. B. Huang, Y. Z. Wu and X. P. Hao, *Chemsuschem*, 2018, **11**, 3198-3207.
3. Y. Wang, Y. Sun, F. Yan, C. L. Zhu, P. Gao, X. T. Zhang and Y. J. Chen, *J. Mater. Chem. A*, 2018, **6**, 8479-8487.
4. W. Hua, H. Sun, H. Liu, Y. Li and J.-G. Wang, *Appl. Surf. Sci.*, 2021, **540**, 148407.
5. A. P. Wu, Y. Xie, H. Ma, C. G. Tian, Y. Gu, H. J. Yan, X. M. Zhang, G. Y. Yang and H. G. Fu, *Nano Energy*, 2018, **44**, 353-363.
6. Y. Gu, S. Chen, J. Ren, Y. A. Jia, C. M. Chen, S. Komarneni, D. J. Yang and X. D. Yao, *Acs Nano*, 2018, **12**, 245-253.
7. B. Fei, Z. L. Chen, J. X. Liu, H. B. Xu, X. X. Yan, H. L. Qing, M. Chen and R. B. Wu, *Adv. Energy Mater.*, 2020, **10**.
8. C. Zhu, Z. Yin, W. Lai, Y. Sun, L. Liu, X. Zhang, Y. Chen and S.-L. Chou, *Adv. Energy Mater.*, 2018, **8**, 1802327.
9. Z. K. Kou, T. T. Wang, Q. L. Gu, M. Xiong, L. R. Zheng, X. Li, Z. H. Pan, H. Chen, F. Verpoort, A. K. Cheetham, S. C. Mu and J. Wang, *Adv. Energy Mater.*, 2019, **9**.
10. M. Zhao, W. Li, J. Y. Li, W. H. Hu and C. M. Li, *Adv Sci*, 2020, **7**.
11. A. P. Tiwari, Y. Yoon, T. G. Novak, K. S. An and S. Jeon, *Acs Appl Nano Mater*, 2019, **2**, 5061-5070.
12. G. Li, J. Yu, W. Yu, L. Yang, X. Zhang, X. Liu, H. Liu and W. Zhou, *Small*, 2020, **16**, 2001980.
13. L. Lei, D. Huang, C. Zhang, R. Deng, S. Chen and Z. Li, *J. Catal.*, 2020, **385**, 129-139.
14. C. Ray, S. C. Lee, B. J. Jin, A. Kundu, J. H. Park and S. C. Jun, *J. Mater. Chem. A*, 2018, **6**, 4466-4476.
15. H. Sun, C. Tian, G. Fan, J. Qi, Z. Liu, Z. Yan, F. Cheng, J. Chen, C.-P. Li and M. Du, *Adv Funct Mater*, 2020, **30**, 1910596.
16. J. Diao, Y. Qiu, S. Liu, W. Wang, K. Chen, H. Li, W. Yuan, Y. Qu and X. Guo, *Adv. Mater.*, 2020, **32**, 1905679.
17. D. Liu, H. Ai, J. Li, M. Fang, M. Chen, D. Liu, X. Du, P. Zhou, F. Li, K. H. Lo, Y. Tang, S. Chen, L. Wang, G. Xing and H. Pan, *Adv. Energy Mater.*, 2020, **10**, 2002464.
18. Z. Wang, L. Xu, F. Huang, L. Qu, J. Li, K. A. Owusu, Z. Liu, Z. Lin, B. Xiang, X. Liu, K. Zhao, X. Liao, W. Yang, Y.-B. Cheng and L. Mai, *Adv. Energy Mater.*, 2019, **9**, 1900390.

19. F. Lin, Z. Dong, Y. Yao, L. Yang, F. Fang and L. Jiao, *Adv. Energy Mater.*, 2020, **10**, 2002176.
20. W. J. Chu, Z. J. Shi, Y. D. Hou, D. N. Ma, X. Bai, Y. F. Gao and N. J. Yang, *ACS Appl. Mater. Interfaces*, 2020, **12**, 2763-2772.
21. T. Zhang, K. N. Yang, C. Wang, S. Y. Li, Q. Q. Zhang, X. J. Chang, J. T. Li, S. M. Li, S. F. Jia, J. B. Wang and L. Fu, *Adv. Energy Mater.*, 2018, **8**.
22. Y. Ha, L. X. Shi, X. X. Yan, Z. L. Chen, Y. P. Li, W. Xu and R. B. Wu, *ACS Appl. Mater. Interfaces*, 2019, **11**, 45546-45553.
23. L. An, J. Feng, Y. Zhang, R. Wang, H. Liu, G.-C. Wang, F. Cheng and P. Xi, *Adv Funct Mater*, 2019, **29**, 1805298.
24. Z. Kang, H. Guo, J. Wu, X. Sun, Z. Zhang, Q. Liao, S. Zhang, H. Si, P. Wu, L. Wang and Y. Zhang, *Adv Funct Mater*, 2019, **29**, 1807031.
25. X. Luo, P. X. Ji, P. Y. Wang, R. L. Cheng, D. Chen, C. Lin, J. A. Zhang, J. W. He, Z. H. Shi, N. Li, S. Q. Xiao and S. C. Mu, *Adv. Energy Mater.*, 2020, **10**.
26. X. Y. Zhao, H. Liu, Y. Rao, X. X. Li, J. L. Wang, G. S. Xia and M. B. Wu, *ACS Sustain. Chem. Eng.*, 2019, **7**, 2610-2618.
27. J. W. Li, Q. N. Zhuang, P. M. Xu, D. W. Zhang, L. C. Wei and D. S. Yuan, *Chinese J Catal*, 2018, **39**, 1403-1410.
28. H. H. Gu, W. Fan and T. X. Liu, *Nanoscale Horiz.*, 2017, **2**, 277-283.
29. D. Zhao, M. Dai, H. Liu, K. Chen, X. Zhu, D. Xue, X. Wu and J. Liu, *Adv. Mater. Interfaces*, 2019, **6**, 1901308.
30. S. Czioska, J. Wang, X. Teng and Z. Chen, *ACS Sustain. Chem. Eng.*, 2018, **6**, 11877-11883.
31. E. Hu, Y. Feng, J. Nai, D. Zhao, Y. Hu and X. W. Lou, *Energy Environ. Sci.*, 2018, **11**, 872-880.
32. B. Wang, S. Jiao, Z. Wang, M. Lu, D. Chen, Y. Kang, G. Pang and S. Feng, *J. Mater. Chem. A*, 2020, **8**, 17202-17211.
33. X. P. Han, W. Zhang, X. Y. Ma, C. Zhong, N. Q. Zhao, W. B. Hu and Y. D. Deng, *Adv. Mater.*, 2019, **31**.
34. Y. Lin, K. A. Sun, S. J. Liu, X. M. Chen, Y. S. Cheng, W. O. Cheong, Z. Chen, L. R. Zheng, J. Zhang, X. Y. Li, Y. Pan and C. Chen, *Adv. Energy Mater.*, 2019, **9**.
35. L. Yu, Q. Zhu, S. Song, B. McElhenny, D. Wang, C. Wu, Z. Qin, J. Bao, Y. Yu, S. Chen and Z. Ren, *Nat. Commun.*, 2019, **10**, 5106.
36. V. R. Jothi, K. Karuppasamy, T. Maiyalagan, H. Rajan, C. Y. Jung and S. C. Yi, *Adv. Energy Mater.*, 2020, **10**.
37. Y. Kuang, M. J. Kenney, Y. Meng, W.-H. Hung, Y. Liu, J. E. Huang, R. Prasanna, P. Li, Y. Li, L. Wang, M.-C. Lin, M. D. McGehee, X. Sun and H. Dai, *Proceedings of the National Academy of Sciences*, 2019, **116**, 6624-6629.
38. F. Dionigi, T. Reier, Z. Pawolek, M. Gliech and P. Strasser, *Chemsuschem*, 2016, **9**, 962-972.
39. S. H. Hsu, J. W. Miao, L. P. Zhang, J. J. Gao, H. M. Wang, H. B. Tao, S. F. Hung, A. Vasileff, S. Z. Qiao and B. Liu, *Adv. Mater.*, 2018, **30**.
40. Y. Zhao, B. Jin, Y. Zheng, H. Jin, Y. Jiao and S.-Z. Qiao, *Adv. Energy Mater.*, 2018, **8**, 1801926.
41. Y. Zhao, B. Jin, A. Vasileff, Y. Jiao and S.-Z. Qiao, *J. Mater. Chem. A*, 2019, **7**, 8117-8121.
42. L. Yu, L. Wu, S. Song, B. McElhenny, F. Zhang, S. Chen and Z. Ren, *Acs Energy Lett*, 2020, **5**, 2681-2689.
43. A. R. Jadhav, A. Kumar, J. Lee, T. Yang, S. Na, J. Lee, Y. Luo, X. Liu, Y. Hwang, Y. Liu and H. Lee, *J. Mater. Chem. A*, 2020, **8**, 24501-24514.