

Selectivity of oxygen evolution reaction on carbon cloth - supported δ -MnO₂ nanosheets in electrolysis of real seawater



Figure S1. MnO₂/CC



Figure S2. Real seawater collection site

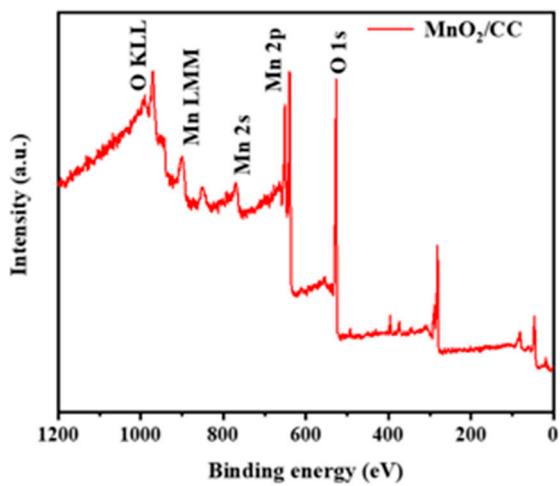


Figure S3. XPS full spectra of MnO₂/CC

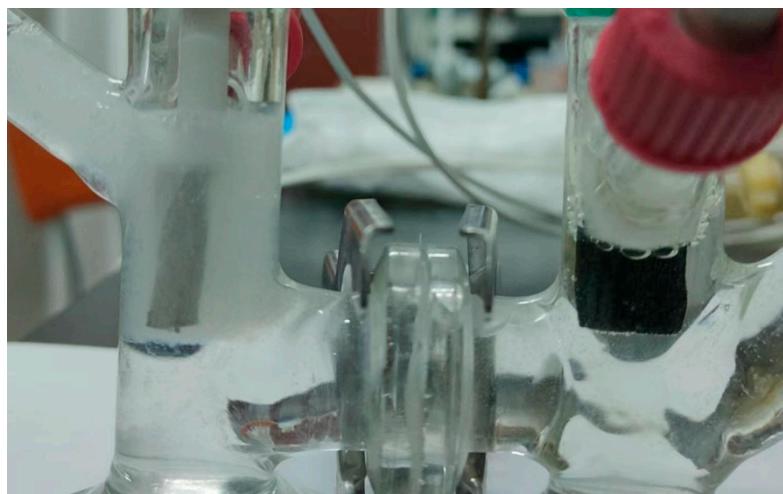


Figure S4. White precipitates are produced at the cathode during electrolysis of seawater

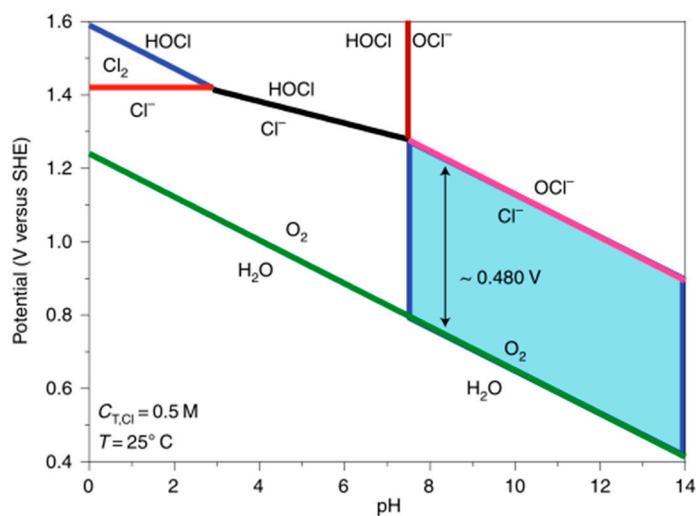


Figure S5. The Pourbaix diagram of an aqueous saline electrolyte [36].

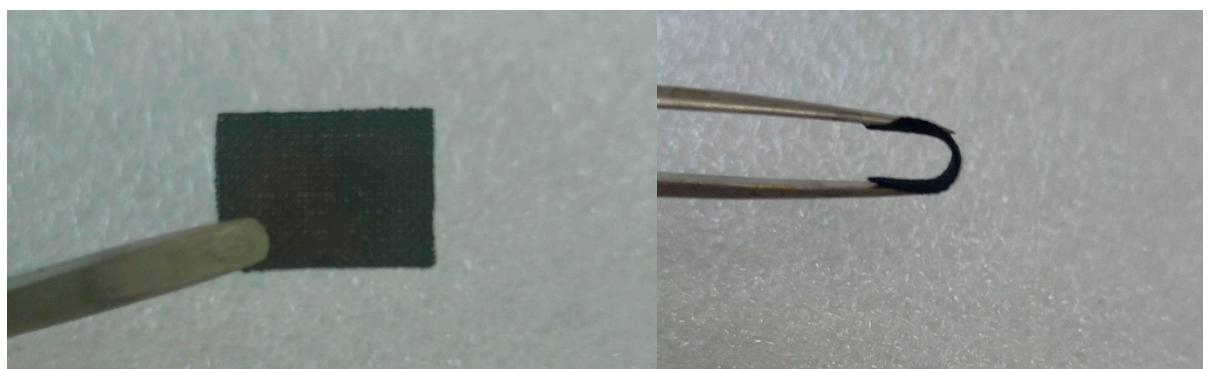


Figure S6. Constant current electrolysis experiment at the end of MnO_2/CC

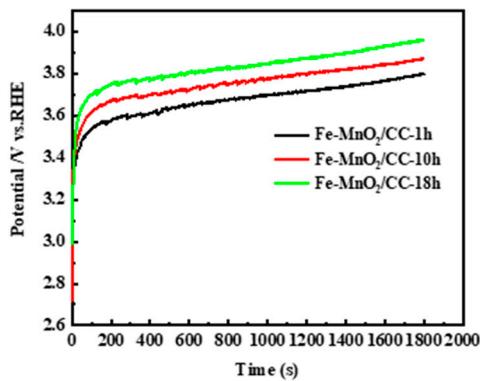


Figure S7. V-t curve of Fe-MnO₂/CC sample with intercalation time of 1h, 10h and 18h at constant current of 100 mA.

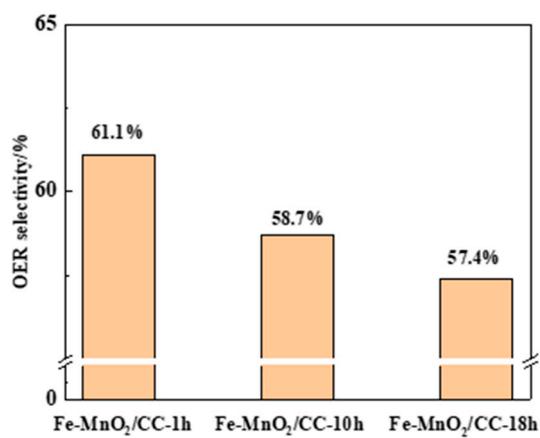


Figure S8. Fe-MnO₂/CC oxygen evolution selectivity histogram at different intercalation times

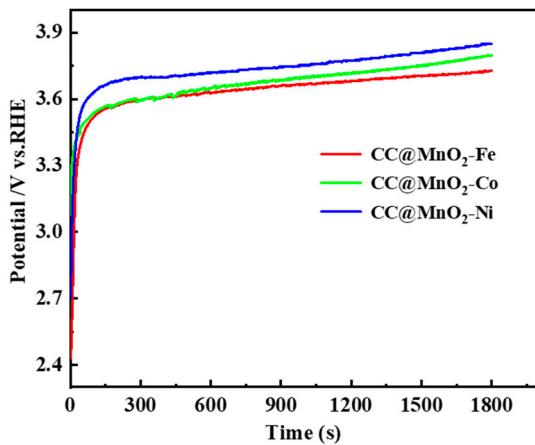


Figure S9. V-t curves of Fe-MnO₂/CC, Co-MnO₂/CC, Ni-MnO₂/CC samples at constant current of 100 mA.

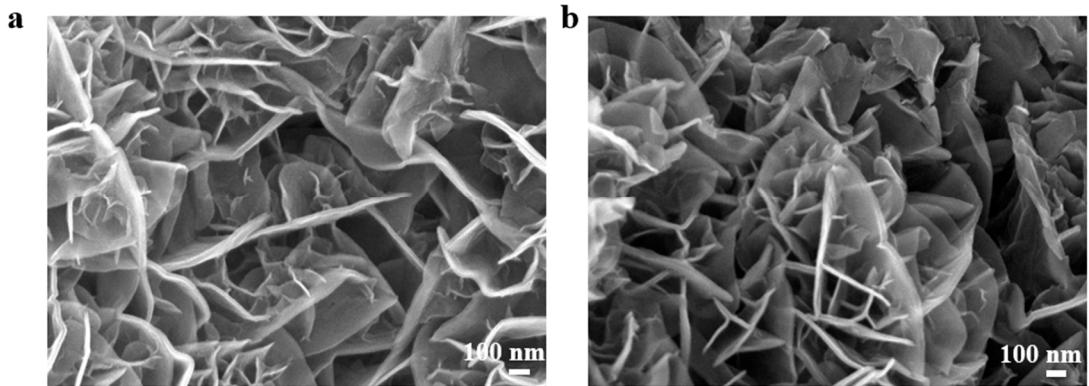


Figure S10. (a) SEM image of MnO₂/CC after electrochemical test; (b) SEM image of Fe-MnO₂/CC after electrochemical test.

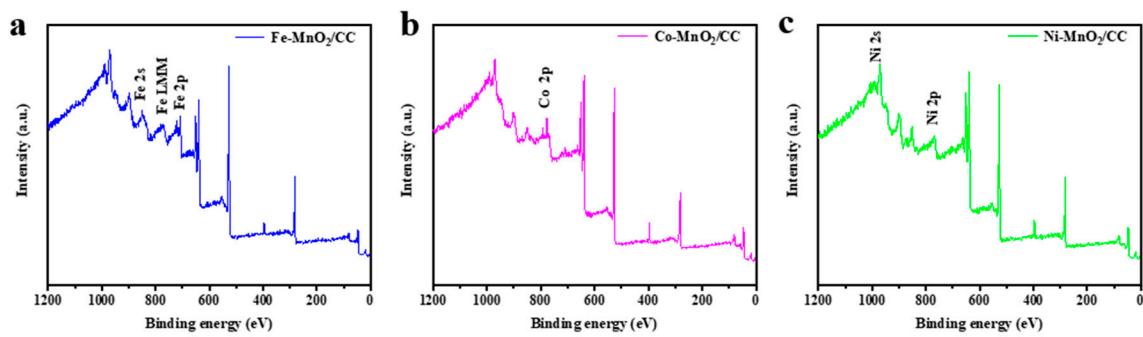


Figure S11. (a) XPS full spectra of Fe-MnO₂/CC; (b) XPS full spectra of Co-MnO₂/CC; (c) XPS full spectra of Ni-MnO₂/CC.

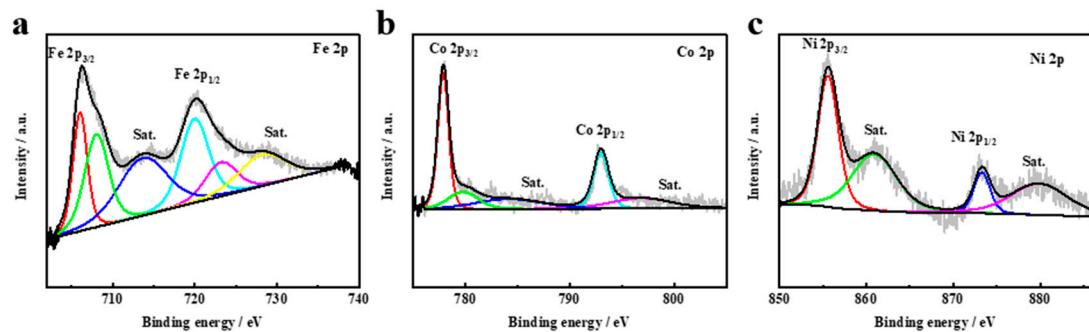


Figure S12. (a) High resolution Fe 2p XPS spectra of Fe-MnO₂/CC; (b) High resolution Co 2p XPS spectra of Co-MnO₂/CC; (c) High resolution Ni 2p XPS spectra of Ni-MnO₂/CC.

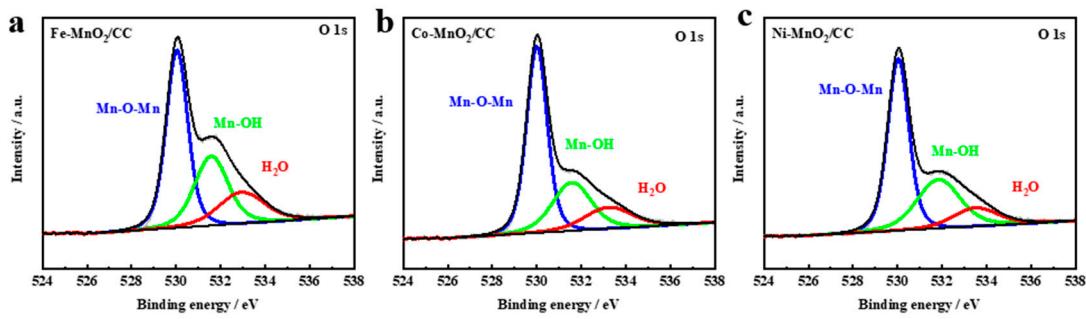


Figure S13. (a)High resolution O 1S XPS spectra of Fe-MnO₂/CC; (b) High resolution O 1S XPS spectra of Co-MnO₂/CC; (c)High resolution O 1S XPS spectra of Ni-MnO₂/CC.

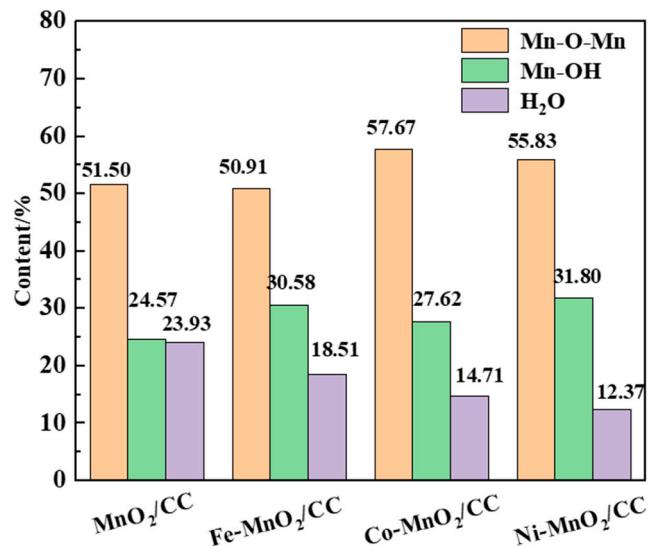


Figure S14. The contents of Mn-O-Mn, Mn-OH and H₂O in MnO₂/CC, Fe-MnO₂/CC, Co-MnO₂/CC and Ni-MnO₂/CC

Table S1. Binding energy corresponding to Mn(III), Mn(IV) peak positions in MnO₂/CC Mn2P high-resolution XPS spectra.

species	Binding energy(eV)	
	Mn 2p _{3/2}	Mn 2p _{1/2}
+3	641.86	653.57
+4	643.14	654.82

Table S2. Binding energy corresponding to Mn(III), Mn(IV) peak positions in Fe-MnO₂/CC, Co-MnO₂/CC and Ni-MnO₂/CC Mn2P high-resolution XPS spectra.

Sample	species	Binding energy(eV)	
		Mn 2p _{3/2}	Mn 2p _{1/2}
Fe-MnO ₂ /CC	+3	642.19	653.68
	+4	643.16	655.06
Co-MnO ₂ /CC	+3	642.08	653.84
	+4	643.38	654.91
Ni-MnO ₂ /CC	+3	642.15	653.74
	+4	643.70	655.04

Table S3. Titration results of solution in tail gas absorption zone after constant current electrolytic seawater test. (Fe-MnO₂/CC-1h)

	1	2	3
Electrolyte volume/mL		10	
KI volume /mL		15	
Initial reading /mL	37.70	32.70	34.70
End reading /mL	45.50	40.70	42.30
Average of Na ₂ SO ₃ consumed/mL		7.80	
nCl ₂ /mol		0.000156	
Total battery /C		180	
Cl ⁻ Oxidation power/C		30.1	

Table S4. Titration results of anodic solution after constant current electrolytic seawater test. (Fe-MnO₂/CC-1h)

	1	2	3
NaOH volume/mL		10	
KI volume /mL		15	
Initial reading /mL	23.80	18.90	21.00
End reading /mL	37.70	32.70	34.70
Average of Na ₂ SO ₃ Consume/mL		13.80	
nCl ₂ /mol		0.000276	
Total battery /C		180	
Cl ⁻ Oxidation power/C		39.9	
Total Cl ⁻ oxidation power/C		70.00	
Cl ⁻ Oxidation ratio /%		38.89	
OER selectivity/%		61.11	

Table S5. Titration results of solution in tail gas absorption zone after constant current electrolytic seawater test. (Fe-MnO₂/CC-10h)

	1	2	3
Electrolyte volume/mL		10	
KI volume /mL		15	
Initial reading /mL	34.00	31.10	33.70
End reading /mL	42.00	39.20	41.60
Average of Na ₂ SO ₃ consumed/mL		8.00	
nCl ₂ /mol		0.00016	
Total battery /C		180	
Cl ⁻ Oxidation power/C		30.9	

Table S6. Titration results of anodic solution after constant current electrolytic seawater test. (Fe-MnO₂/CC-10 h)

	1	2	3
NaOH volume/mL		10	
KI volume /mL		15	
Initial reading /mL	18.90	16.20	18.70
End reading /mL	34.0	31.10	33.70
Average of Na ₂ SO ₃ Consume/mL		15.00	
nCl ₂ /mol		0.003	
Total battery /C		180	
Cl ⁻ Oxidation power/C		43.4	
Total Cl ⁻ oxidation power/C		74.3	
Cl ⁻ Oxidation ratio /%		41.28	
OER selectivity/%		58.72	

Table S7. Titration results of solution in tail gas absorption zone after constant current electrolytic seawater test. (Fe-MnO₂/CC-18h)

	1	2	3
Electrolyte volume/mL		10	
KI volume /mL		15	
Initial reading /mL	39.80	36.40	35.50
End reading /mL	46.80	43.30	42.30
Average of Na ₂ SO ₃ consumed/mL		6.90	
nCl ₂ /mol		0.000138	
Total battery /C		180	
Cl ⁻ Oxidation power/C		26.6	

Table S8. Titration results of anodic solution after constant current electrolytic seawater test. (Fe-MnO₂/CC -18h)

	1	2	3
NaOH volume/mL		10	
KI volume /mL		15	
Initial reading /mL	22.50	19.00	18.30
End reading /mL	39.80	36.40	35.50
Average of Na ₂ SO ₃ Consume/mL		17.30	
nCl ₂ /mol		0.00346	
Total battery /C		180	
Cl ⁻ Oxidation power/C		50.0	
Total Cl ⁻ oxidation power/C		76.6	
Cl ⁻ Oxidation ratio /%		42.56	
OER selectivity/%		57.44	

Table S9. Titration results of solution in tail gas absorption zone after constant current electrolytic seawater test. (MnO₂/CC)

	1	2	3
Electrolyte volume/mL		10	
KI volume /mL		15	
Initial reading /mL	36.90	35.20	36.10
End reading /mL	43.50	41.70	42.50
Average of Na ₂ SO ₃ consumed/mL		6.50	
nCl ₂ /mol		0.00013	
Total battery /C		180	
Cl ⁻ Oxidation power/C		25.0	

Table S10. Titration results of anodic solution after constant current electrolytic seawater test. (MnO₂/CC)

	1	2	3
NaOH volume/mL		10	
KI volume /mL		15	
Initial reading /mL	24.80	22.70	23.80
End reading /mL	36.90	35.20	36.10
Average of Na ₂ SO ₃ Consume/mL		12.30	
nCl ₂ /mol		0.000276	
Total battery /C		180	
Cl ⁻ Oxidation power/C		35.6	
Total Cl ⁻ oxidation power/C		60.6	
Cl ⁻ Oxidation ratio /%		33.67	
OER selectivity/%		66.333	

Table S11. Titration results of solution in tail gas absorption zone after constant current electrolytic seawater test. (Co-MnO₂/CC-1h)

	1	2	3
Electrolyte volume/mL		10	
KI volume /mL		15	
Initial reading /mL	34.50	35.40	34.80
End reading /mL	42.40	43.70	42.90
Average of Na ₂ SO ₃ consumed/mL		8.10	
nCl ₂ /mol		0.000162	
Total battery /C		180	
Cl ⁻ Oxidation power/C		31.4	

Table S12. Titration results of anodic solution after constant current electrolytic seawater test. (Co-MnO₂/CC-1h)

	1	2	3
NaOH volume/mL		10	
KI volume /mL		15	
Initial reading /mL	20.10	21.20	20.50
End reading /mL	34.50	35.40	34.80
Average of Na ₂ SO ₃ Consume/mL		14.30	
nCl ₂ /mol		0.000286	
Total battery /C		180	
Cl ⁻ Oxidation power/C		42.2	
Total Cl ⁻ oxidation power/C		73.6	
Cl ⁻ Oxidation ratio /%		40.90	
OER selectivity/%		59.10	

Table S13. Titration results of solution in tail gas absorption zone after constant current electrolytic seawater test. (Ni-MnO₂/CC-1h)

	1	2	3
Electrolyte volume/mL		10	
KI volume /mL		15	
Initial reading /mL	33.30	34.40	39.70
End reading /mL	39.50	40.80	46.30
Average of Na ₂ SO ₃ consumed/mL		6.40	
nCl ₂ /mol		0.000128	
Total battery /C		180	
Cl ⁻ Oxidation power/C		24.7	

Table S14. Titration results of anodic solution after constant current electrolytic seawater test. (Ni-MnO₂/CC -1h)

	1	2	3
NaOH volume/mL		10	
KI volume /mL		15	
Initial reading /mL	19.50	20.60	25.90
End reading /mL	33.30	34.40	39.70
Average of Na ₂ SO ₃ Consume/mL		13.80	
nCl ₂ /mol		0.000276	
Total battery /C		180	
Cl ⁻ Oxidation power/C		40.1	
Total Cl ⁻ oxidation power/C		64.8	
Cl ⁻ Oxidation ratio /%		36.00	
OER selectivity/%		64.00	