

## Electronic Supplementary Information

### Constructing NiMnS electrode with Mn-rich surface for hydrogen production in anion exchange membrane water electrolyzer

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Table S1. Atomic ratios and contents of NiS/Ti and NiMnS/Ti, obtained via XPS analysis.

Catalyst	Atomic ratio (%)		
	Ni	S	Mn
NiS/Ti	72.7	27.3	0
NiMnS/Ti	61.7	11.7	26.6

Table S2. Performance comparison (at 50 °C) of the proposed AEMWE and existing frameworks.

MEA configurations (anode    cathode)	Current density (A/cm <sup>2</sup> )	Cell voltage (V)	Electrolyte	Reference
IrO <sub>2</sub> /CP    NiMnS/Ti	0.9	2.0	1.0 M KOH	This work
Cu <sub>0.75</sub> Co <sub>2.25</sub> O <sub>4</sub>    NiCoO- NiCo/C	0.5	2.0	1.0 M KOH	[1]
IrOx    Platinum Black	0.5	2.29	1.0 M KOH	[2]
Ir black    NiMo/X72	1.0	1.9	1.0 M KOH	[3]
Ir    NiCu MMO/C	0.7	1.9	1.0 M KOH	[4]
Cu <sub>0.81</sub> Co <sub>2.19</sub> O <sub>4</sub> NS/NF    Co <sub>3</sub> O <sub>4</sub> NS/NF	0.43	2.0	1.0 M KOH	[5]

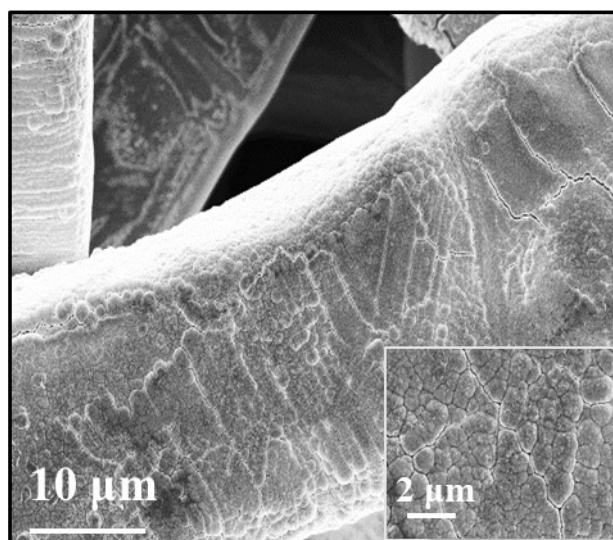


Figure S1. FE-SEM images of NiMn/Ti

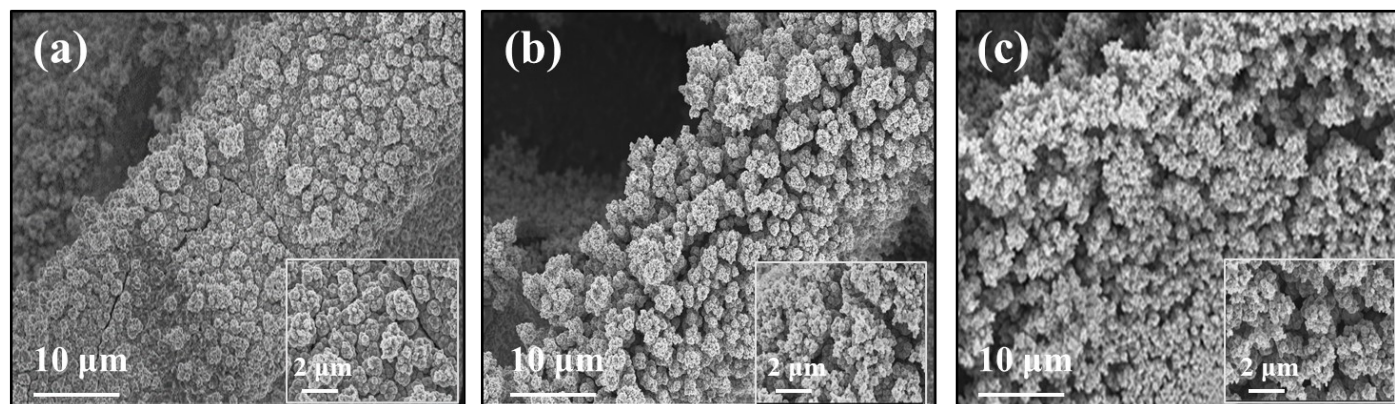


Figure S2. FE-SEM images of NiMnS/Ti electrodeposited for (a) 10 min, (b) 15 min, (c) 30 min

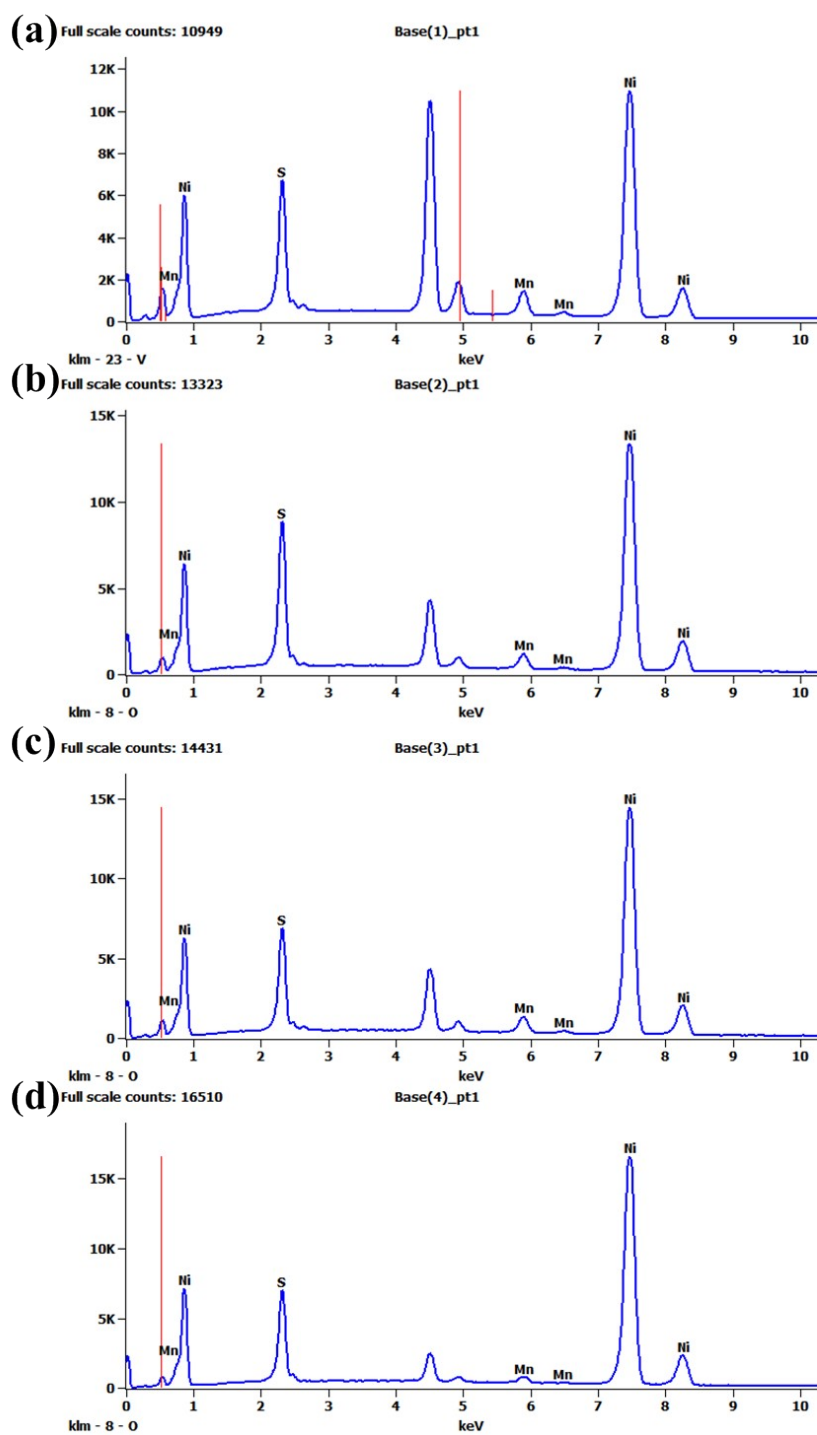


Figure S3. EDS spectra of NiMnS electrodeposited for (a) 10 min, (b) 15 min, (c) 20 min, (d) 30 min

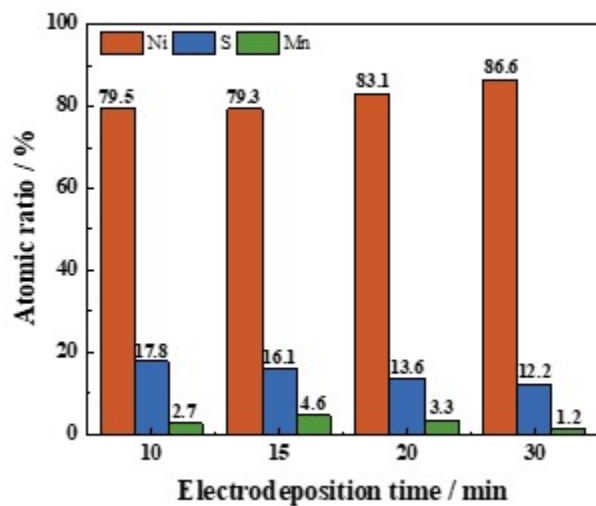


Figure S4. Atomic ratios of Ni, S, and Mn in NiMnS/Ti electrodeposited for 10, 15, 20, and 30 min, obtained from EDS analyses.

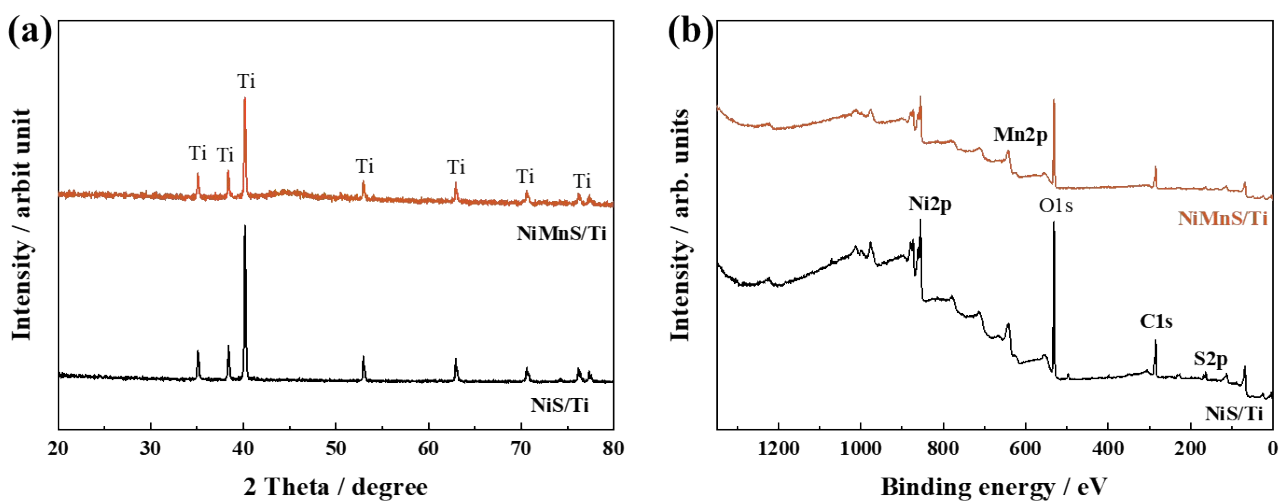


Figure S5. (a) XRD patterns and (b) XPS survey spectra of NiS/Ti and NiMnS/Ti.

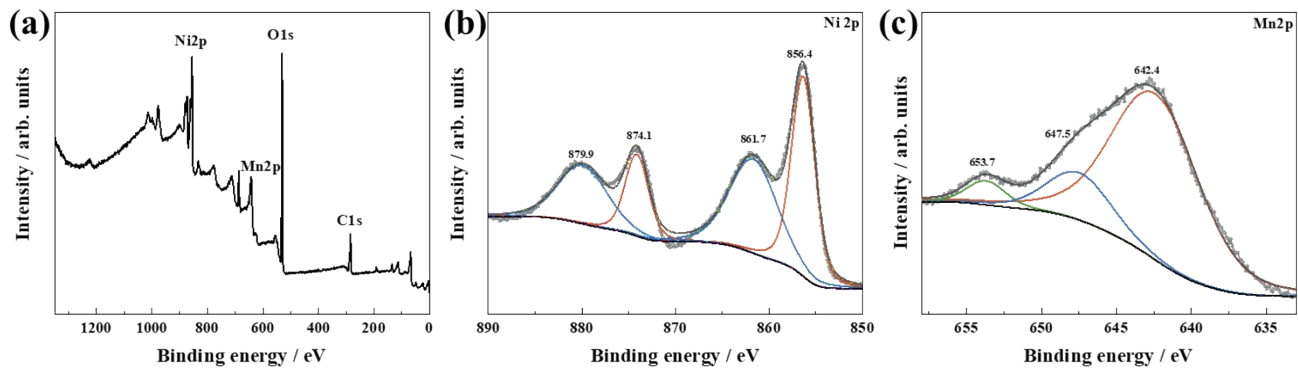


Figure S6. XPS profiles of NiMn/Ti: (a) survey spectra, (b) Ni 2p, (c) Mn 2p.

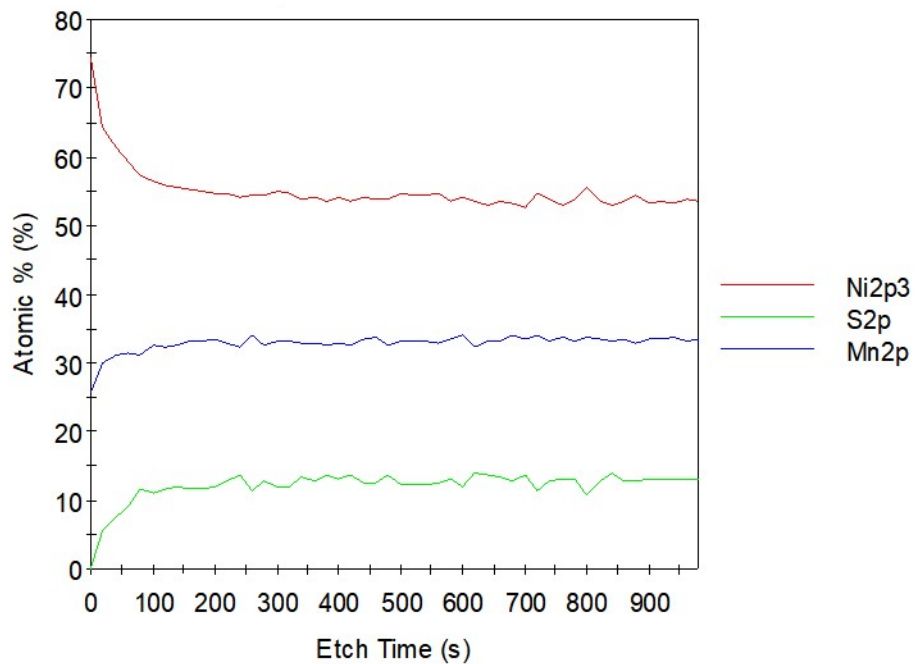


Figure S7. Atomic (%) profiles of Ni 2p, S 2p, and Mn 2p during etching.

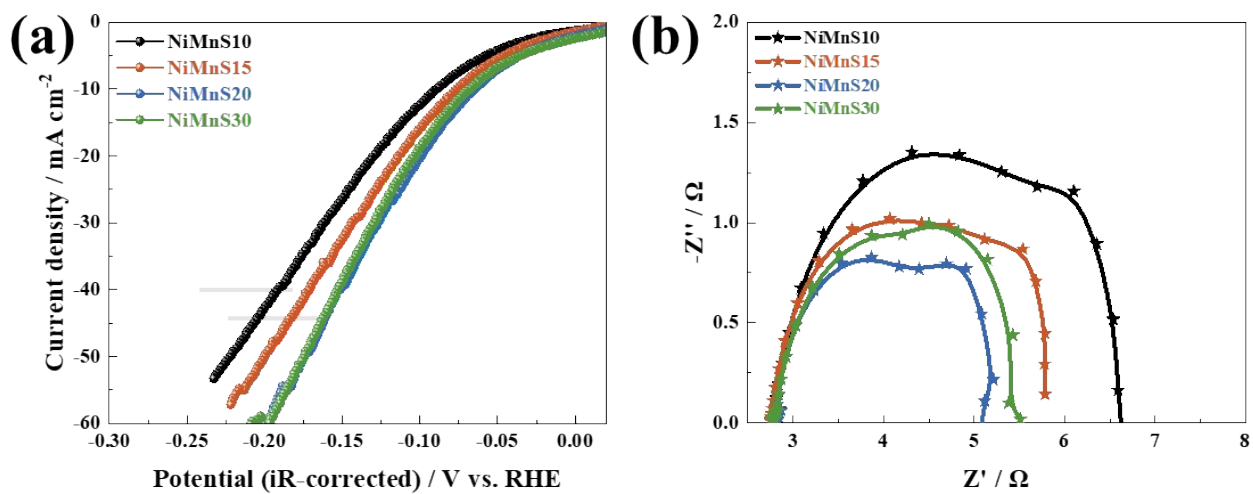


Figure S8. Electrochemical properties of NiMnS/Ti electrodeposited for 10, 15, 20, and 30 min:

(a) HER activity, (b) Nyquist plots at  $-10 \text{ mA/cm}^2$ .

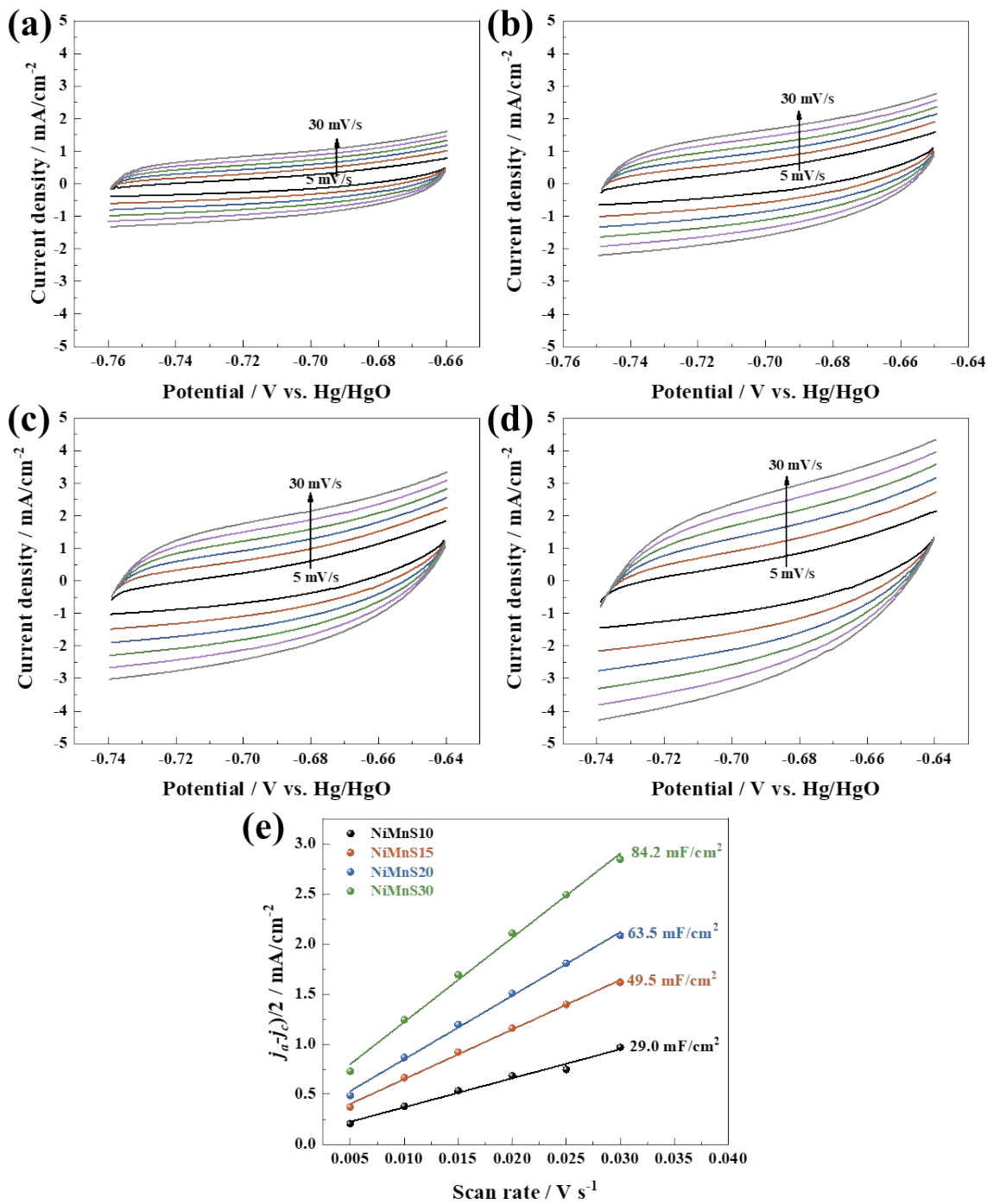


Figure S9. Repeated CV curves from values measured in 1.0 M KOH for NiMnS/Ti electrodeposited for :  
 (a) 10 min, (b) 15 min, (c) 20 min, and (d) 30 min, and (e) corresponding  $C_{dl}$  values.



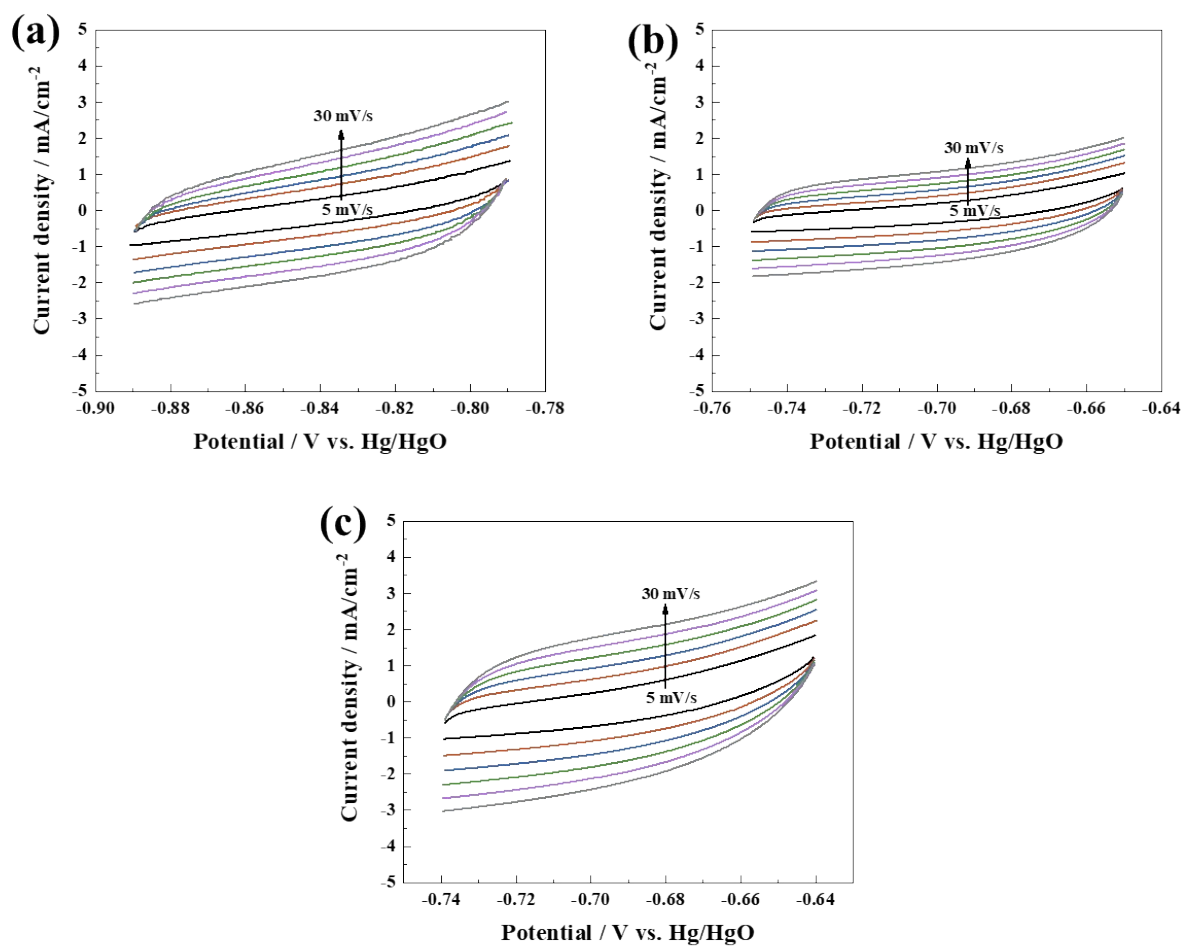


Figure S10. Repeated CV curves from values measured in 1.0 M KOH for (a) NiMn/Ti, (b) NiS/Ti, (c) NiMnS/Ti.

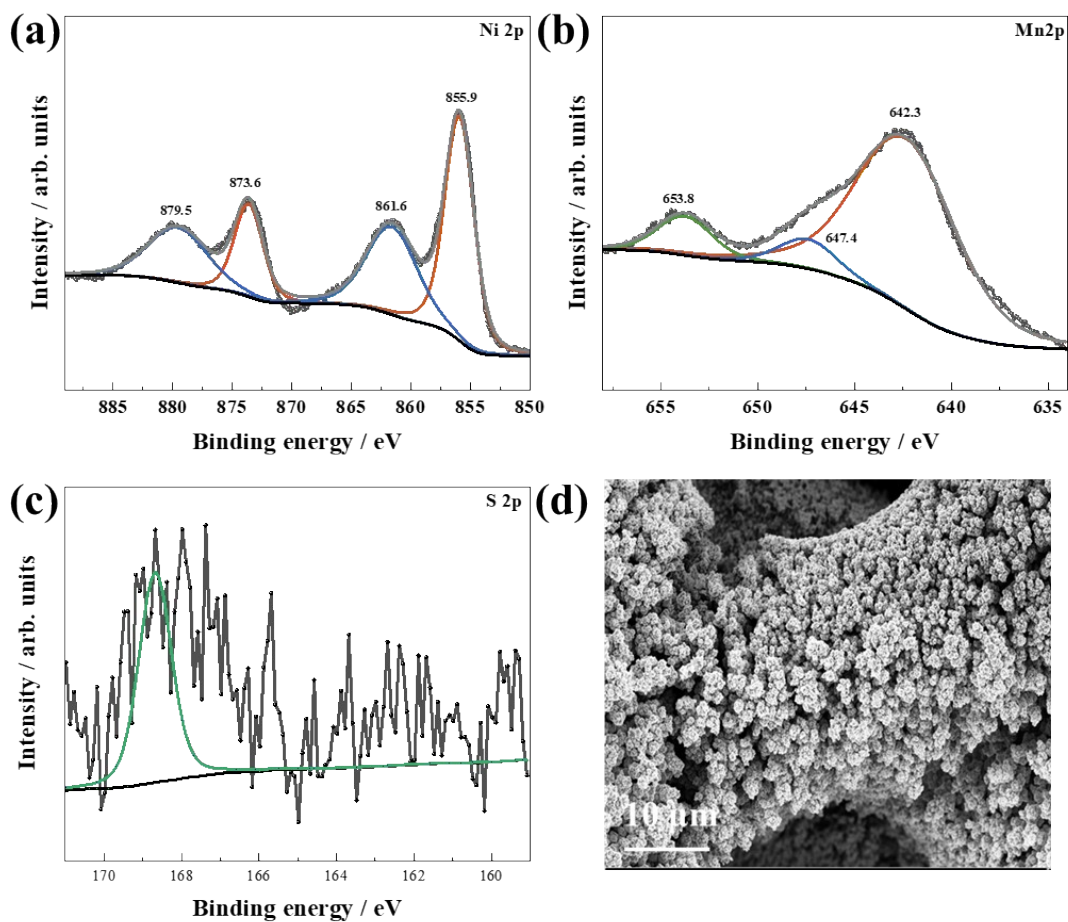


Figure S11. XPS spectra of (a) Ni 2p, (b) Mn 2p (c) S 2p and FE-SEM image (d) of NiMnS/Ti after 24 h of chronopotentiometry measurement.

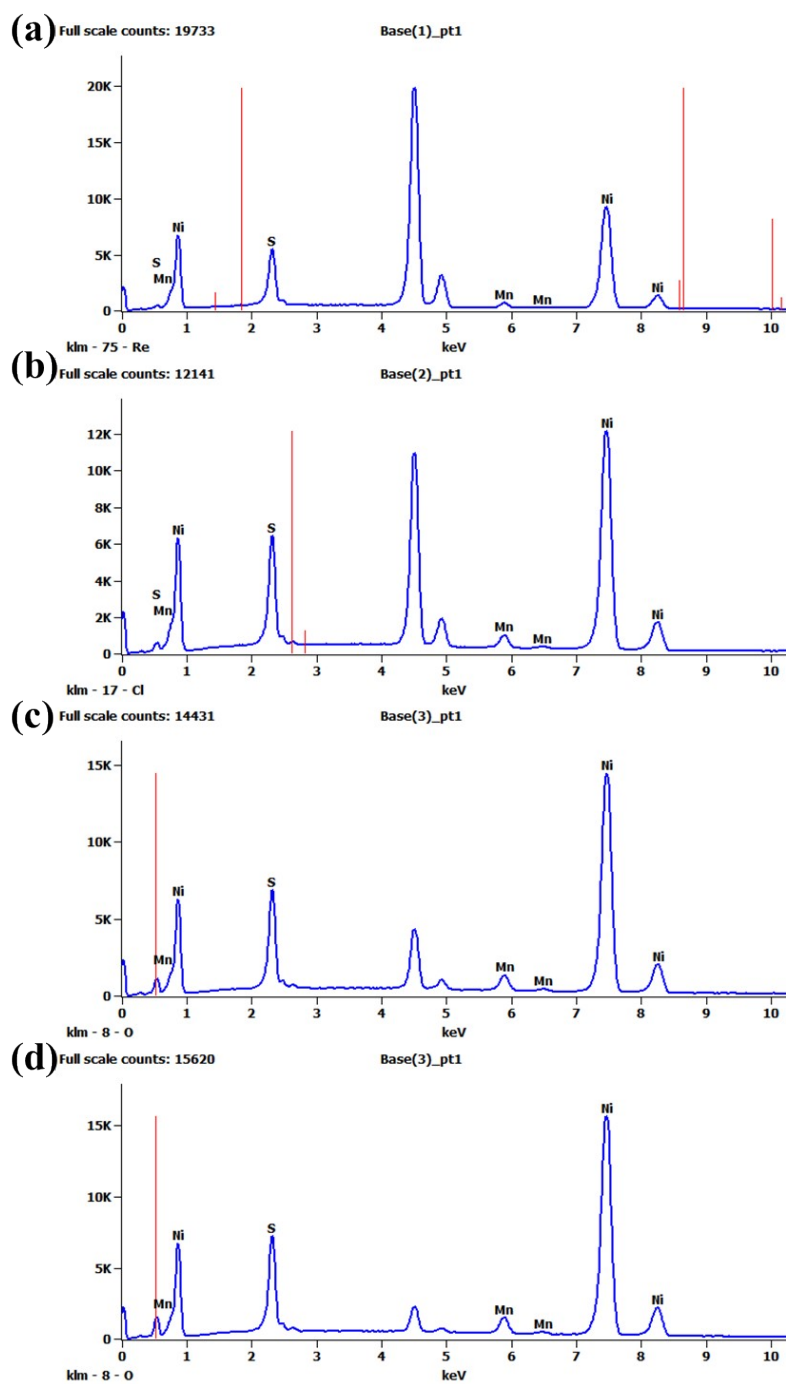


Figure S12. EDS spectra of NiMnS/Ti electrodeposited with different concentrations of  $Mn^{2+}$ : (a) 20 mM, (b) 30 mM, (c) 40 mM, (d) 50 mM.

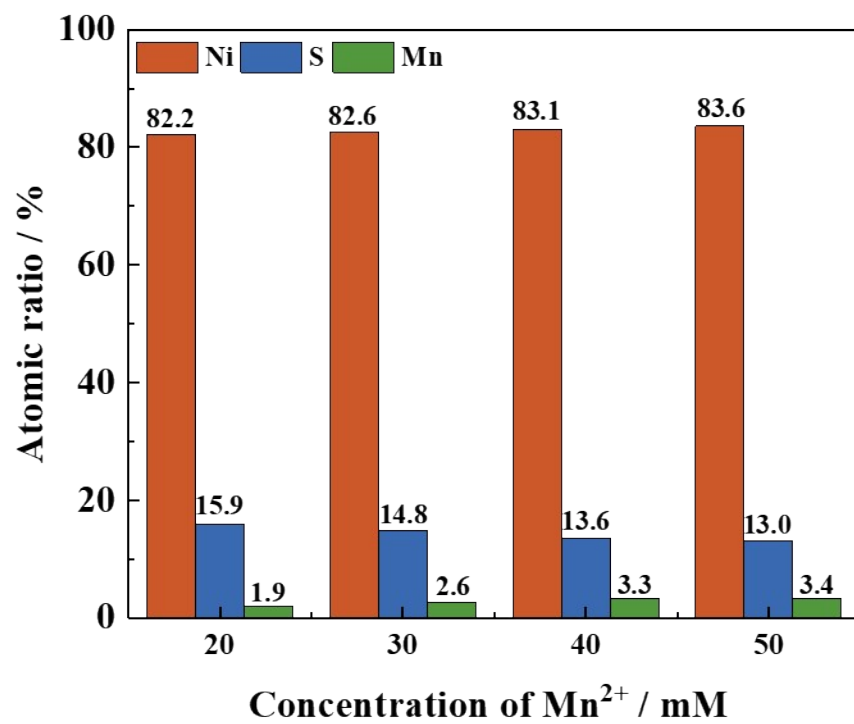


Figure S13. Atomic ratios of Ni, S, and Mn in NiMnS/Ti electrodeposited with different concentrations of Mn<sup>2+</sup>, obtained from EDS analyses.

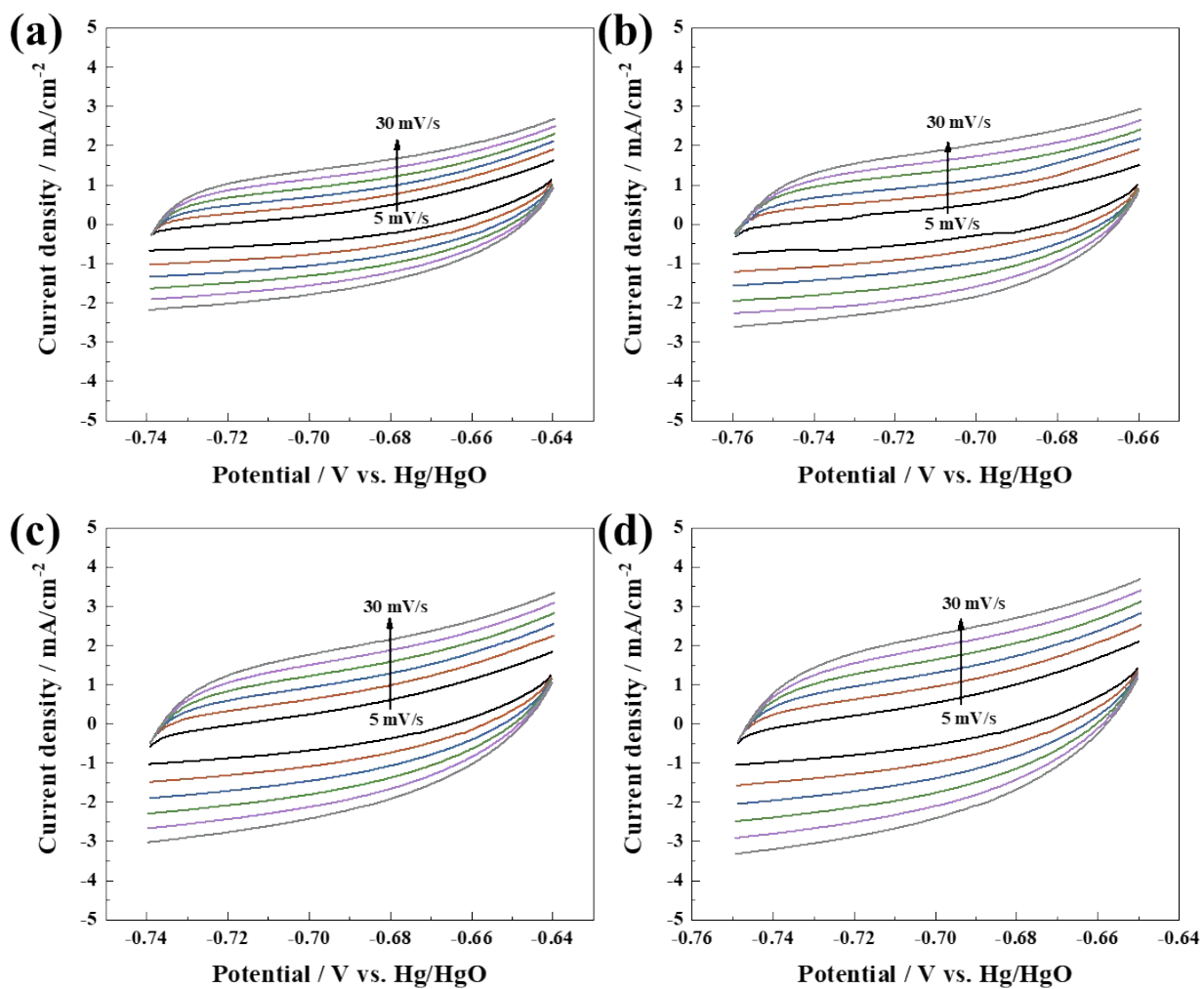


Figure S14. Repeated CV curves from values measured in 1.0 M KOH for NiMnS/Ti electrodeposited with different concentrations of  $Mn^{2+}$ : (a) 20 mM, (b) 30 mM, (c) 40 mM, (d) 50 mM.

## References

1. Y.S. Park, et al., Commercial anion exchange membrane water electrolyzer stack through non-precious metal electrocatalysts. *Appl. Catal. B: Environ.* 2021;292:120170.
2. D. Xu, et al., Earth-abundant oxygen electrocatalysts for alkaline anion-exchange-membrane water electrolysis: Effects of catalyst conductivity and comparison with performance in three-electrode cells. *ACS Catal.* 2018;9:7–15.
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4. W. Guo, et al., Cu–Co–P electrodeposited on carbon paper as an efficient electrocatalyst for hydrogen evolution reaction in anion exchange membrane water electrolyzers. *Int. J. Hydrog. Energy.* 2021;46:19789–19801.
5. Y.S. Park, et al., Co<sub>3</sub>S<sub>4</sub> nanosheets on Ni foam via electrodeposition with sulfurization as highly active electrocatalysts for anion exchange membrane electrolyzer. *Int. J. Hydrog. Energy.* 2020;45: 36–45.