

Supplementary Information

Asymmetric structure tuning of industrial MnO₂ arrays on hierarchical lead-based anode for manganese metallurgy

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This Supplementary Information includes:

S1 Experimental

S2 Supporting Figures S1 to S17

S3 Supporting Table S1-S4

Experimental

Preparation of hierarchical LBA

1) TiB₂ interlayer prepared by plasma spraying.

Fixed the polished Pb-0.9%Ag (LBA) matrix on the working platform of plasma spraying machine, which was immediately followed by spraying TiB₂ powder at atmosphere along periodic reciprocating path. The core parameters of atmospheric plasma spraying (APS) were listed in **Table S1**.

2) Synthesis of γ -MnO₂ catalytic film on LBA/TiB₂ surface.

The synthesis of γ -MnO₂ was carried out in a glass three-electrode system through anodic oxidation. The above LBA/TiB₂ were utilized as working electrodes, saturated calomel electrode (SCE: 0.24 V vs. SHE) and graphite rod were used as the reference and counter electrodes, respectively. Electrolyte were prepared by dissolving 0.728 mol MnSO₄·H₂O and 0.408 mol H₂SO₄ in 1 L DI water under magnetic stirring. The electrodeposition was performed at 95°C over a constant anodic current density of 3 mA/cm². The total coulomb during MnO₂ deposition were fixed at 7.085 C/cm².

Preparation of Pb-adopted MnO₂

Add 5g Mn(NO₃)₂ solution (50% wt%) to 50 ml of deionized water. Then, the 0, 0.6, 3, and 6 ml of 0.5 mol/L Pb(NO₃)₂ solution were added to the above solution respectively. Stir the mixture continuously for 20 minutes at 40°C in a water bath to ensure uniform mixing. After that, titrate with 0.2 mol/L KMnO₄ solution dropwise until excess is reached, and continue stirring for 4 hours. After filtration, dry samples in 60°C oven for 12 hours, followed by grinding. Transfer these samples to a tube furnace and calcine it at 400°C for 4

hours. Allow it to cool naturally to obtain γ -MnO₂ samples with various Pb-adopted.

Electrochemical experimental

The various Pb-adopted MnO₂ were loaded on glassy carbon (GC) electrode, and the oxygen evolution kinetics performance is tested in a 1M KOH solution. The LSV tests were performed at potentials ranging from 0.2 V to 0.9 V at a scan rate of 10 mV/s with 400 rpm. The ECSA estimated by the electrochemical double-layer capacitance (C_{DL}) can serve as a crucial criterion for comparing the activity of samples. First, the non-Faradaic current (i_c) was measured at four scan rates ($v=5, 10, 20, 40, \text{ and } 80 \text{ mV/s}$) between 0.0 V to 0.1 V which determined by CV analysis in quiescent condition.

The rotating ring-disk electrode (RRDE) technique is employed to calculate the Faradaic efficiency (FE), which represents the proportion of transferred electrons used for oxygen evolution in the net reaction. The ring potential (-0.7V vs. SCE) for RRDE studies was chosen based on the oxygen reduction reaction (ORR) voltammograms recorded on the Pt ring in the O₂-saturated 1 M KOH solution. The disk potential was set for a linear scan within the range of 0.3-0.9 V at a scan rate of 10 mV/s. Additionally, multiple potential steps are applied within the range of 0.5-0.7 V, incrementing by 25 mV every 60 seconds.

To test the activity and stability of the anode, a series of scatter monotonically decreasing potentials were applied to each electrode for 90 s to collect the steady-state current except for that the initial point was held for 180 s to further minimize any pseudo-capacitance. Additionally, a current density of 40 mA/cm² was applied for 4 hours to different anodes in electrolytes containing Mn²⁺ or without Mn²⁺. During data collecting, auxiliary electrochemical impedance spectroscopy (EIS) technique was applied to compensate the

solution resistance (R_s).

Theoretical calculations

All the spin-polarization periodic density functional theory (DFT) calculations were performed within the frame of Vienna ab initio simulation package (VASP). In terms of electronic structure of γ -MnO₂, DFT+U method was performed. According to previous studies, the U values for Mn is 3.9 eV. The projector augmented wave (PAW) method was used to represent the core-valence electron interaction. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional was employed to model the electron exchange-correlation. The energy cutoff of 450 eV was adopted, and a $3 \times 3 \times 1$ k -point with a G-centered k mesh was used in the calculation. Structure optimization was to relax until the forces of all atoms were less than 0.02 eV/Å.

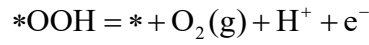
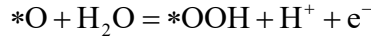
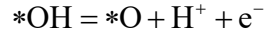
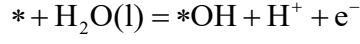
Meanwhile, we calculated the electronic structure of Pb-ion-doped γ -MnO₂ in different forms to facilitate an atomic-scale understanding of doping. We also explored the binding energy of Pb at different doping sites. The formula used for binding energy calculations is as follows:

$$E_b = E_{bulk+Pb} - (E_{bulk} + E_{Pb})$$

Here, $E_{bulk+Pb}$ represents the total cohesive energy when a metal atom is doped into γ -MnO₂, E_{bulk} represents the cohesive energy of pure-phase γ -MnO₂, and E_{Pb} represents the energy of one Pb atom. The (210) crystal face was selected as the characteristic exposed crystal face based on XRD and TEM diffraction results.

For the construction of the adsorption free energy step model for OER, in this study, the

(210) surface was designated as the adsorption crystal face. Meanwhile, only the adsorption oxygen mechanism, considered as the main step of the OER reaction, was taken into account, where the OER mechanism in the acidic solution of the target system is as follows:



The adsorption energy formulas for *OH, *O, and *OOH can be directly obtained from the above equation as follows::

$$\Delta G(1) = G(*\text{OH}) + G(\text{H}^+) + eU - G(*) - G(\text{H}_2\text{O})$$

$$\Delta G(2) = G(*\text{O}) + G(\text{H}^+) + eU - G(*\text{OH})$$

$$\Delta G(3) = G(*\text{OOH}) + G(\text{H}^+) + eU - G(*\text{O}) + G(\text{H}_2\text{O})$$

$$\Delta G(4) = G(\text{O}_2) + G(*) + G(\text{H}^+) + eU - G(*\text{OOH})$$

Where $e = -1$, U is the applied electrode potential set to 1.23 V (vs. SHE), and thus $eU = -1.23$ eV. The energy of liquid water molecules is considered equivalent to that of gaseous water molecules at their saturation vapor pressure. $G(\text{H}^+)$ and eU can be converted from $G(\text{H}_2)$, and since the VASP program cannot accurately calculate the molecular energy of O_2 , it is necessary to convert the free energy of $G(\text{O}_2)$ through $G(\text{H}_2)$:

$$2G(\text{H}_2\text{O}) - 2G(\text{H}_2) - G(\text{O}_2) = -4.92\text{eV}$$

For the free energy calculations of each step mentioned above, a correction is applied by computing the frequencies of surface-adsorbed molecules. The corrected free energy is calculated as follows:

$$\Delta G = \Delta E - \Delta \text{ZPE} - T\Delta S + \Delta G_U$$

Here, ΔZPE represents the zero-point vibrational energy, $T\Delta S$ is the entropy correction, and ΔG_U is equal to eU , where U is the mentioned potential of 1.23 V.

Long term Galvanostatic polarization:

Galvanostatic electrowinning was performed at 313 K in a 5 L Plexiglas cell consisting of anode and cathode compartments separated by a polyester diaphragm. The catholyte composition was maintained at Mn^{2+} (15 g/L), $(\text{NH}_4)_2\text{SO}_4$ (130 g/L) and SeO_2 (40/20 mg/L). The active area of aluminum cathode (304#, 200 cm^2) was identical to anode (200 cm^2), and the distance between the anode and cathode was fixed at 30 mm. The peristaltic pump was used to pump the fresh electrolyte into cathode chamber to maintain a stable catholyte composition. Waste electrolyte overflows from the top of the anode chamber. During the electrodeposition process, the Mn^{2+} and free H^+ of catholyte was monitored by chemical titration at a fixed time interval, and the change in anode potential is recorded using a potentiometer. Every 24 hours of electrodeposition at an applied current of 7 A, the cathode plate is removed, washed, and then weighed after drying for 10 hours in an oven at 343 K. The anode sludge is thoroughly cleaned with DI water and collected after drying in the same manner.

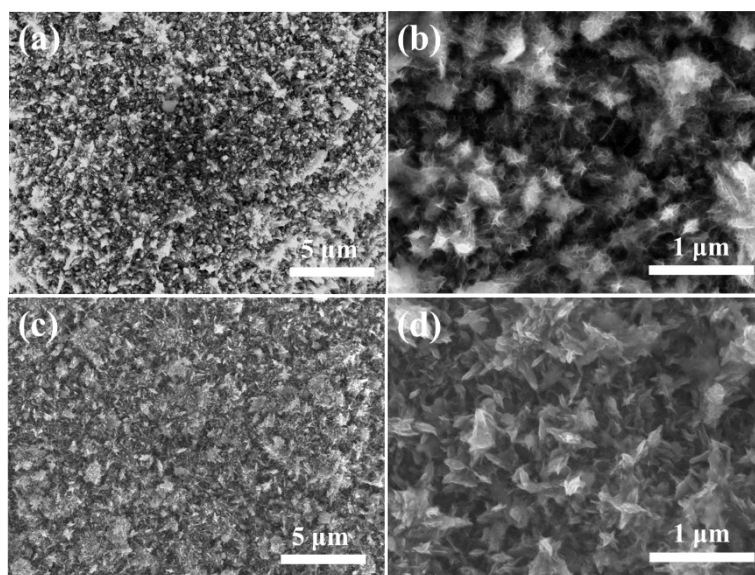


Figure S1 The SEM images of MnO₂ layer on different substrates: (a-b) TDL and (c-d) LBA.

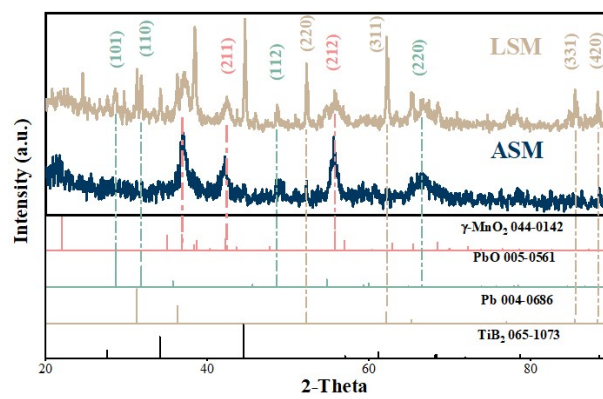


Figure S2 XRD patterns of LSM and ASM.

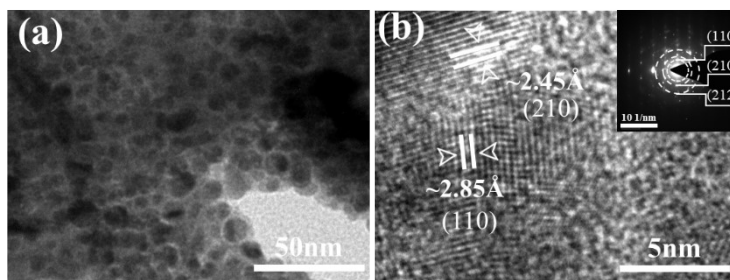


Figure S3 (a) TEM, (b) HRTEM and SAED of LSM.

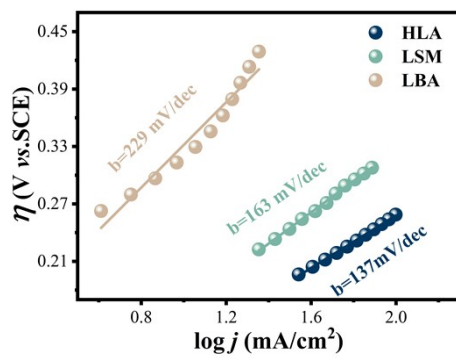


Figure S4 The Tafel slope of various anodes.

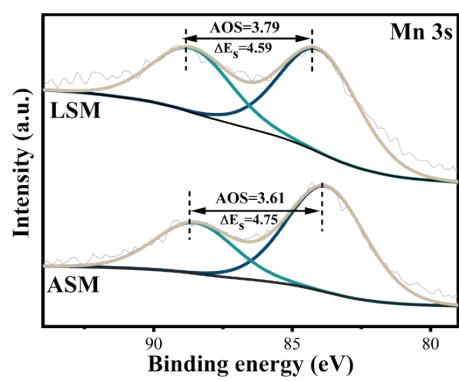


Figure S5 XPS fine spectra of Mn 3s of LSM and ASM.

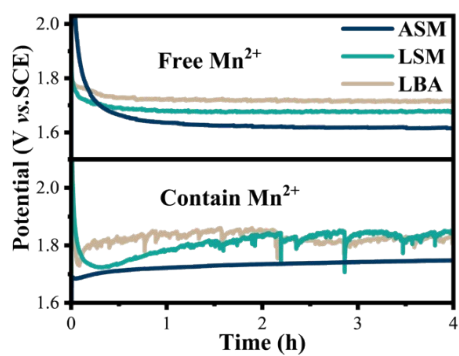


Figure S6 The 4h galvanostatic polarization of various electrodes during Mn²⁺ contain or free in electrolyte under 40 mA/cm² anodic current density.

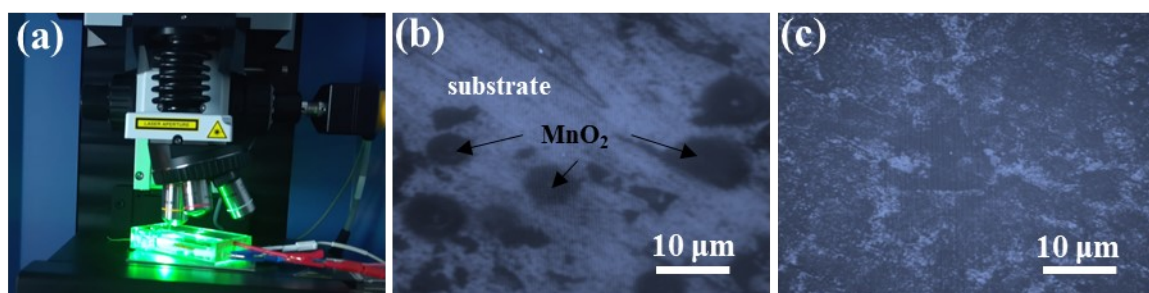


Figure S7 (a) The self-designed electrochemical *in-situ* Raman system. The optical microscope image of the working electrode surface with MnO_2 loading after (b) 1 min and (c) 10 min of electrodeposition.

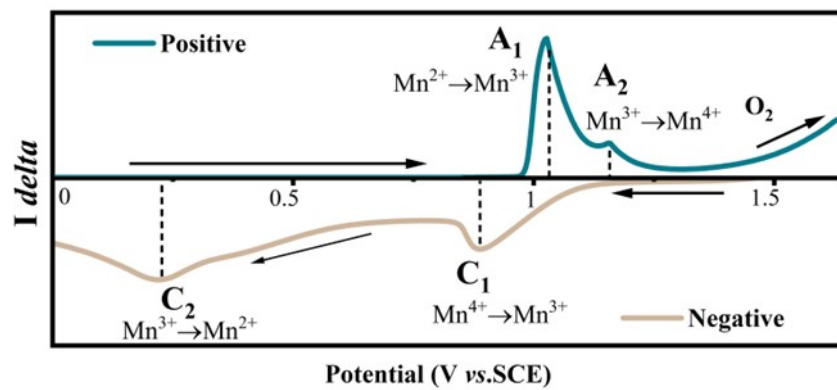


Figure S8 The REDOX pathway of Mn^{2+} tested by SWV curve.

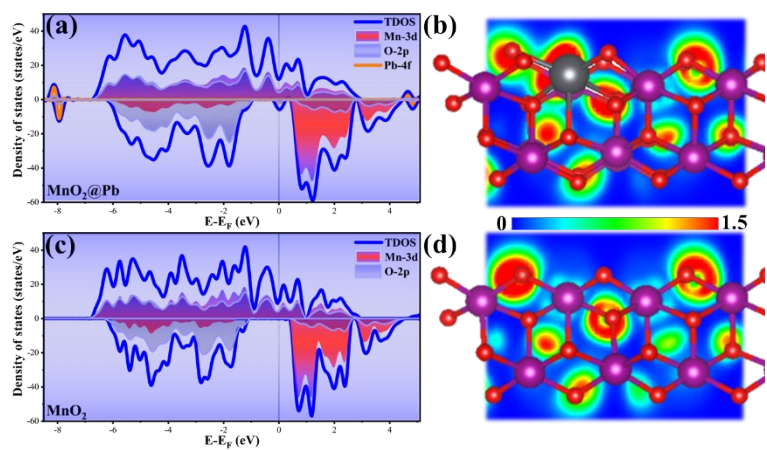


Figure S9 The DOS and ELF of (a-b) MnO₂@Pb and (c-d) MnO₂.

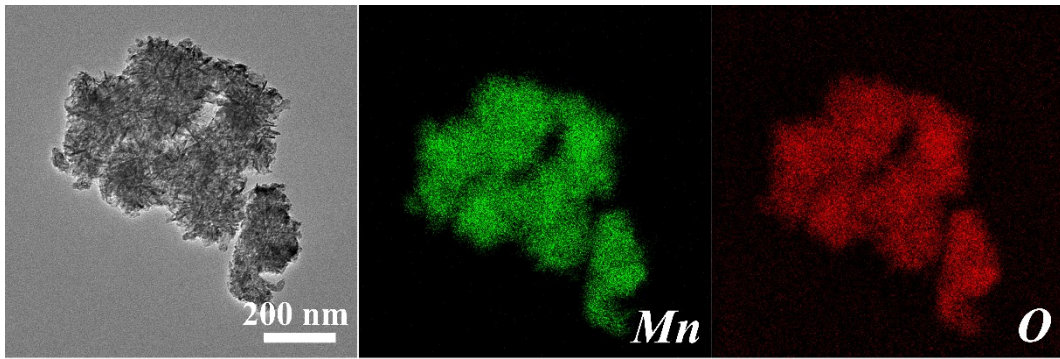


Figure S10 TEM and mapping of pure MnO_2 .

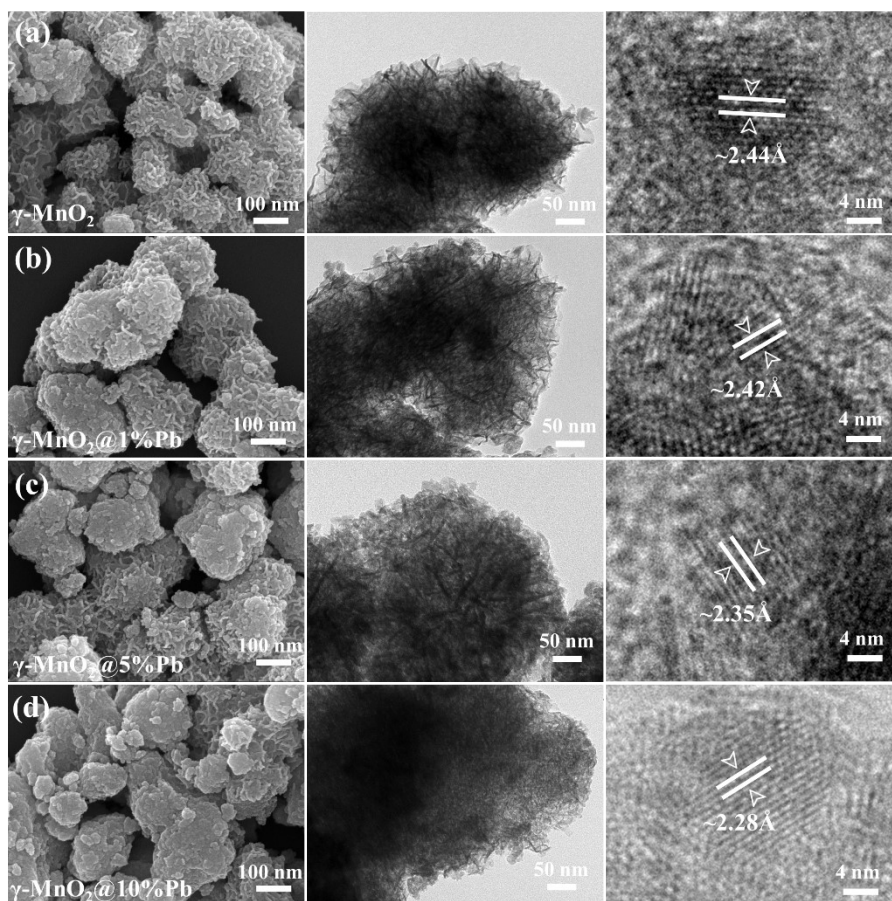


Figure S11 The images of SEM, TEM of various Pb-adopted MnO₂: (a) pure MnO₂; (b) MnO₂@1%Pb; (c) MnO₂@5%Pb; (d) MnO₂@10%Pb.

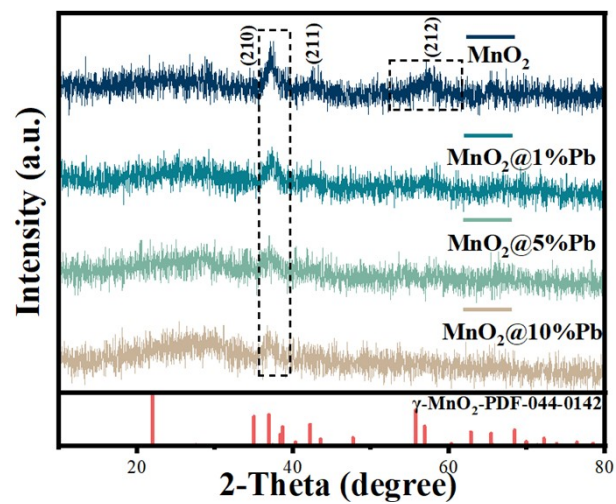


Figure S12 XRD patterns of the various Pb-adopted MnO₂.

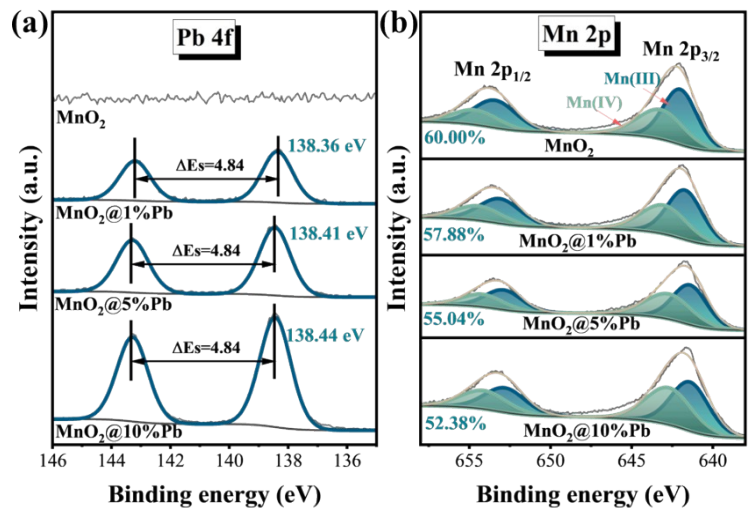


Figure S13 XPS fine spectra of (a) Pb_{4f} and (b) Mn_{2p} of various Pb-adopted MnO₂.

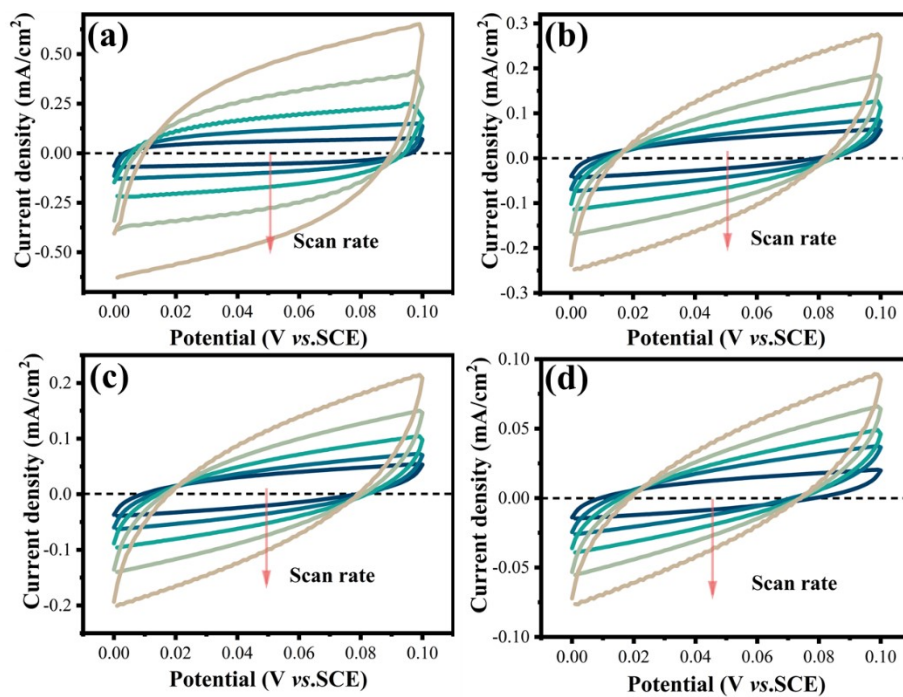


Figure S14 CV curves at different sweep rates of the MnO₂@x%Pb (a-d, x=0, 1, 5 and 10).

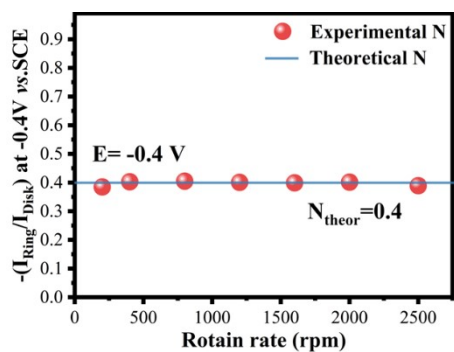


Figure S15 Determination of the ring collection efficiency for a GC-disc and Pt-ring RRDE: ring and disk currents in the 1 M KOH solution containing 10 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ at 10 mV s^{-1} and different rotation rates and the corresponding ring and disk current ratio at $E_{\text{Disk}} = -0.4 \text{ V}$.

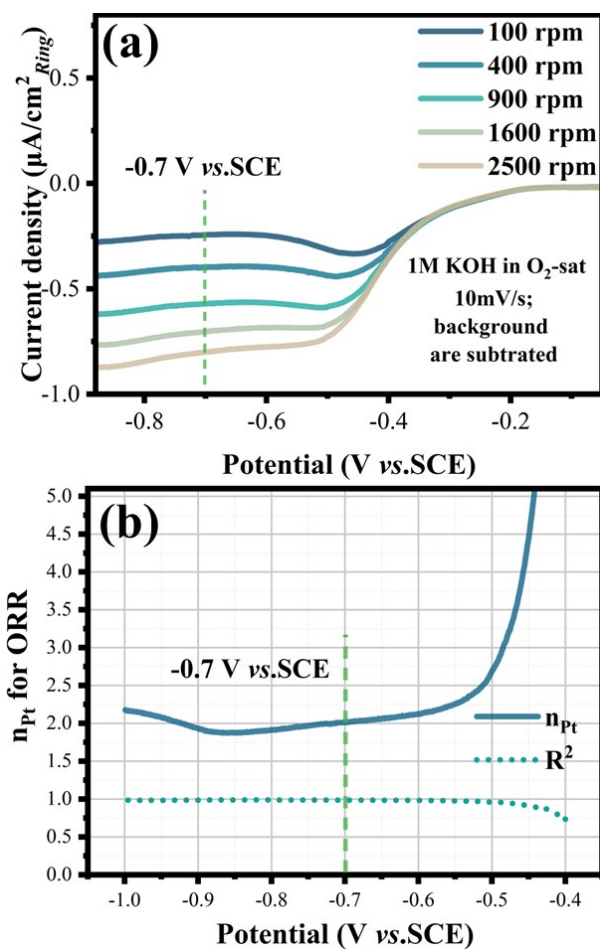


Figure S16 (a) ORR CVs of the Pt ring in the O_2 -saturated 1 M KOH solution at 10 mV s^{-1} and different rotation rates; (b) the number of electrons transferred in the ORR determined by Koutecký-Levich analysis for the ring geometry (solid line) and Pearson correlation coefficient in a thousandth degree (dotted line).

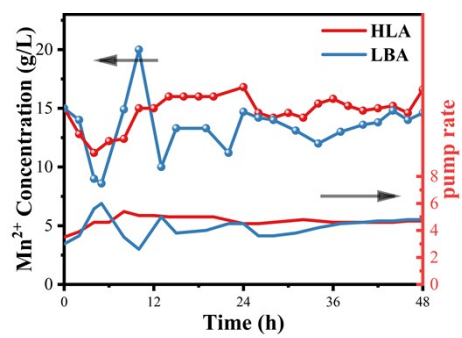


Figure S17 The concentration of Mn²⁺ and peristaltic pump rate.

Table S1 Parameters of APS.

<i>Distance</i> (mm)	<i>Electricity</i> (A)	<i>Argon</i> (cfm)	<i>Hydrogen</i> (cfm)	<i>Voltage</i> (V)	<i>Powder feeding</i> <i>rate</i>	<i>Gun speed</i> (mm/s)	<i>Spraying</i> <i>rounds</i>	<i>Power</i> (kw)
120	360~380	75~80	12~14	120~130	4~6	500	10	250

Table S2 Formation energy of different type of Pb doping in γ -MnO₂ at (210) surface.

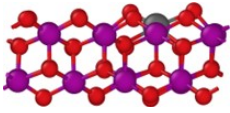
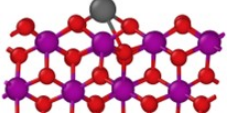
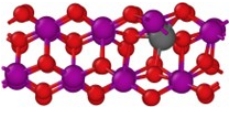
Type of doping	Replaced	Adsorption	Intercalation
Formation energy	-5.24 eV	-2.02 eV	-2.73 eV
Type of doping			

Table S3 Comparison of simulation results of Mn electrodeposition.

Anode plate material	LBA	HLA
Temperature (°C)		35
Electrolyte Composition	130 g/L (NH ₄) ₂ SO ₄ ; 15 g/L Mn ²⁺	
Cathode Plate	304 [#] stainless steels	
Cathode Plate Area (cm ²)		200.00
Cathode Current Density (mA/cm ²)		37.50
Anode Plate Area (cm ²)		66.00
Anode Current Density (mA/cm ²)		56.80
SeO ₂ Concentration (mg/L)	40.00	20.00
Average Daily Manganese Yield (g)	142.10	146.30
Cathodic Current Efficiency (%)	77.02	79.29
Power Consumption (kW·h/t Mn)	5436.62	5258.01
Anode Slime Quantity (g)	120.00	6.60
Average Daily Pb Corrosion (g)	0.87	0.10

Table S4 Mn²⁺ consumption and destination statistics.

	LBA	HLA
Day 1	172.28	151.41
Day 2	174.01	154.12
Total Consumption of Mn ²⁺ (g)	346.29	305.53
Mn in Cathode Production (g)	284.2	292.6
Mn in Anode Slime (g)	78.86	4.21