

Sulfur-Confinement Synthesis of L₁₀-PtZn Intermetallic Catalysts for Enhanced Oxygen Reduction

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Catalyst preparation

Typically, 26.5 mg of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, 6.07 mg of $\text{ZnCl}_2 \cdot 6\text{H}_2\text{O}$, and 6.09 mg of thiourea were dispersed in 20 mL of ultrapure water and ultrasonicated for 5 min to obtain a homogeneous metal salt solution, maintaining a Pt:Zn molar ratio of 2:1. Subsequently, 37 mg of Black Pearl carbon was added as the support, followed by ultrasonication for 1 h to form a uniform suspension. The mixture was then stirred at 60 °C until complete evaporation of water, yielding a smooth slurry, which was further dried in a vacuum oven at 60 °C for 12 h. The dried black solid was thoroughly ground, placed in a tubular furnace, and annealed at 300–800 °C for 2 h under an Ar/ H_2 atmosphere with a heating rate of 5 °C·min⁻¹, followed by natural cooling to room temperature. The resulting catalysts were denoted as PtZn/S-C-T, where *T* represents the reduction/pyrolysis temperature. The PtZn-C catalysts were synthesized with same method.

Catalyst characterization

Transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) images were obtained using a JEOL JEM-2100F operating at 200 kV. X-ray diffraction (XRD) of all synthesized catalysts was performed using a SmartLab-SE diffractometer with Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$). X-ray photoelectron spectroscopy (XPS) results were collected using an AXIS-ULTRA DLD-00W instrument. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was conducted using an Avio 200 instrument. X-ray Absorption Fine Structure (XAFS) measurements at the Pt L₃-edge and Cu K-edge were carried out at the 1W1B beamline of the Beijing Synchrotron Radiation Facility (BSRF), which operates at 2.5 GeV and 250 mA.

Electrochemical performance test

For ink preparation, 3 mg of catalyst was dispersed in 1 mL of 0.1wt.% Nafion solution and ultrasonicated in an isopropanol/water mixture for 1 h. Subsequently, 5 μL of the ink was drop-cast onto a rotating disk electrode (RDE, 5 mm in diameter), yielding a Pt loading of 15 $\mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$. All electrochemical measurements were carried out on a CHI 760E electrochemical workstation using a conventional three-electrode configuration, with the catalyst-coated RDE as the working electrode, a reversible hydrogen electrode (RHE) as the reference electrode, and a Pt wire as the counter electrode. The electrolyte temperature was maintained at 25 °C with a thermostatic water bath.

Cyclic voltammetry (CV) was performed in N_2 -saturated 0.1 M HClO_4 solution within a potential window of 0.05–1.05 V (vs. RHE) at a scan rate of 50 $\text{mV} \cdot \text{s}^{-1}$. Linear sweep voltammetry (LSV) was conducted in O_2 -saturated 0.1 M HClO_4 over the potential range of 0.05–1.05 V (vs. RHE) at a scan rate of 10 $\text{mV} \cdot \text{s}^{-1}$. Accelerated durability tests (ADT) were performed in O_2 -saturated 0.1 M HClO_4 by potential cycling between 0.6 and 1.0 V (vs. RHE) at 100 $\text{mV} \cdot \text{s}^{-1}$ for 30,000 cycles

Fuel cell performance testing

The performance of H_2 - O_2 and H_2 -air fuel cells was evaluated using a commercial Scribner 850e test system with single cells. Membrane electrode assemblies (MEAs) with an active area of 5 cm^2 were fabricated by ultrasonically spraying well-dispersed catalyst ink onto a Nafion HP proton exchange membrane (GORE, 15 μm thickness). Commercial gas diffusion layers

(Sigracet) were then hot-pressed onto both sides of the membrane at 1 MPa for 90 s. The commercial gas diffusion layer (GDL) with a microporous layer and a thickness of 250 μm at 25 kPa (Freudenberg H24CX483) was used. Before the performance testing, the cell was conditioned as follows. The cell temperature was increased to 60°C, and hydrogen and air with an atmospheric pressure were supplied to the anode and cathode, respectively. The relative humidity of the gases was controlled to be 80%, and the flow rates were 0.5 L/min for the anode and 1 L/min for the cathode. After starting the gas supplies, the cell voltage was scanned between 0-1.0 V at the rate of 0.01 V/s for 20 cycles. The H₂-air performance test was performed using a square wave voltage by scanning the voltage from open circuit voltage to 0.2 V with each voltage for 30 s. The Pt loadings were controlled at 0.1 mg·cm⁻² for both the anode (commercial Pt/C, 20 wt% Pt, Johnson Matthey) and the cathode (PtZn catalyst and 20 wt% Pt/C). The single cell was operated at 80 °C with fully humidified H₂/air (150 kPa, 0.5/2.0 mL/min, 100% RH). Prior to performance evaluation, the cell was conditioned by continuous activation. Accelerated stress tests (ASTs) were conducted according to the DOE protocol, with pure H₂ and N₂ supplied to the anode and cathode, respectively. The cell voltage was cycled between 0.6 and 0.95 V in a square-wave profile, with each voltage step maintained for 3 s.

Density functional theory (DFT) calculations

DFT calculations were performed using the Vienna *ab initio* Simulation Package (VASP) with the projector augmented wave (PAW) method. The exchange–correlation interactions were treated within the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) functional, and a plane-wave energy cutoff of 400 eV was applied.

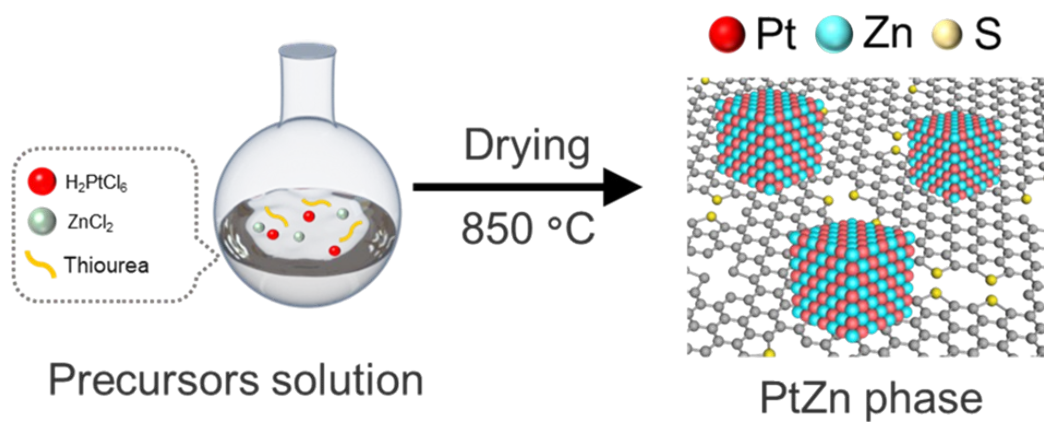


Figure S1. Schematic diagram of L1_0 -PtZn catalyst synthesis

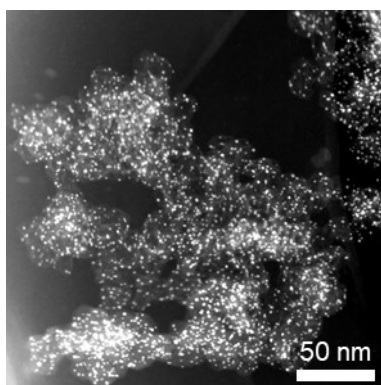


Figure S2. low-magnification TEM images of the PtZn/S-C catalyst.

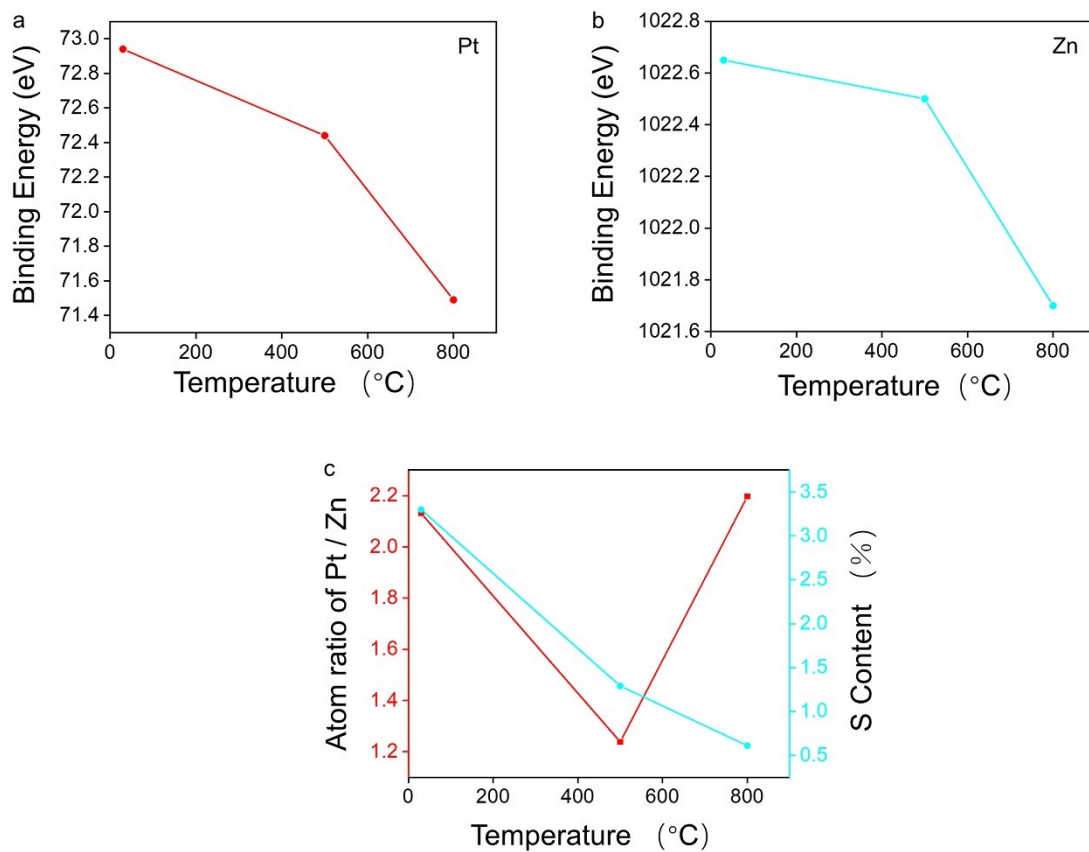


Figure S3. XPS results of Pt $4f$ (a), Zn $2p$ (b) and (c) S content and atom ratio of Pt/Zn with increased temperature.

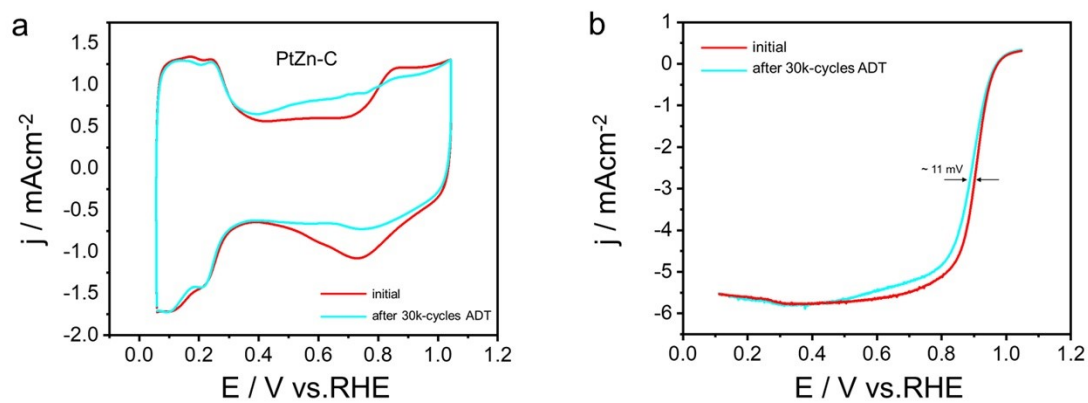


Figure S4. Electrochemical durability of PtZn-C catalyst: (a) CV curves and (b) LSV curves of PtZn-C-850 recorded before and after 30,000 ADT cycles, showing negligible changes in electrochemical features and ORR polarization behavior.

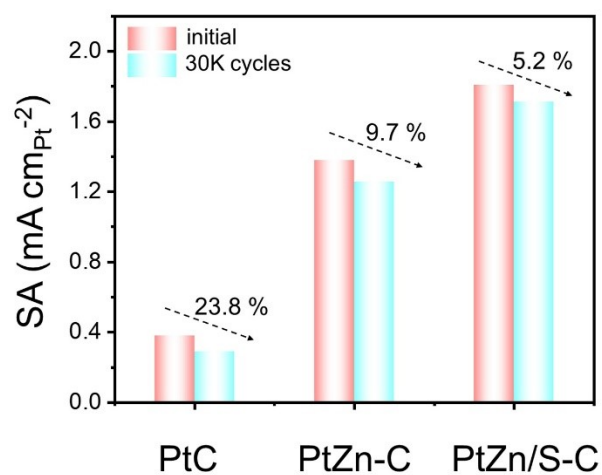


Figure S5. Comparison of specific activities for Pt/C, PtZn-C, PtZn/S-C catalyst after 30, 000 cycles durability test under 0.9 V.

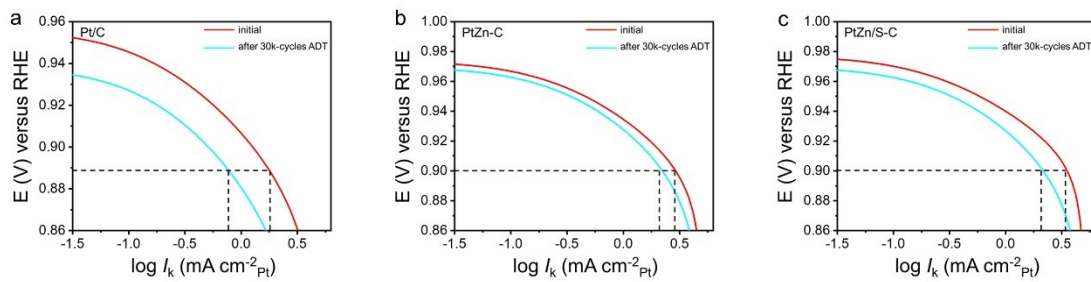


Figure S6. Tafel analysis before and after durability testing: (a), (b) and (c) Tafel plots of commercial Pt/C recorded before and after 30,000 ADT cycles.

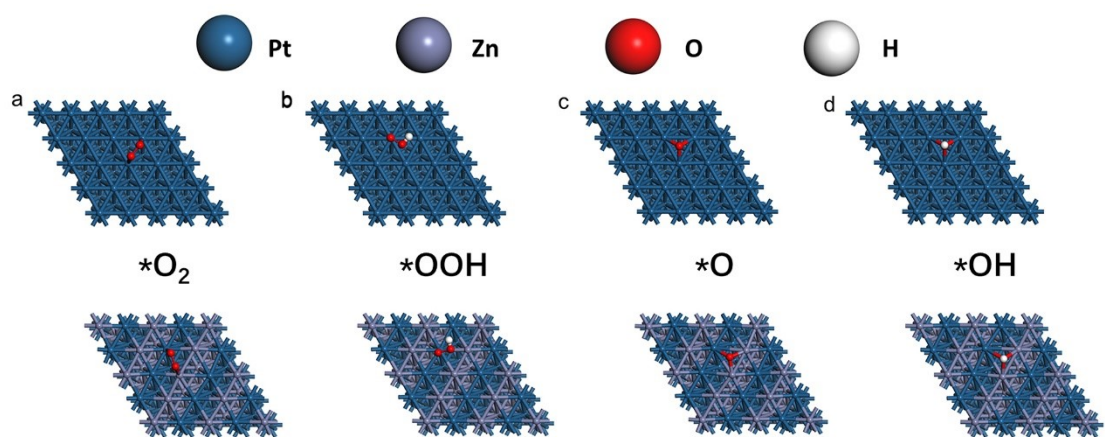


Figure S7. Adsorption/desorption model of oxygen reduction intermediates.

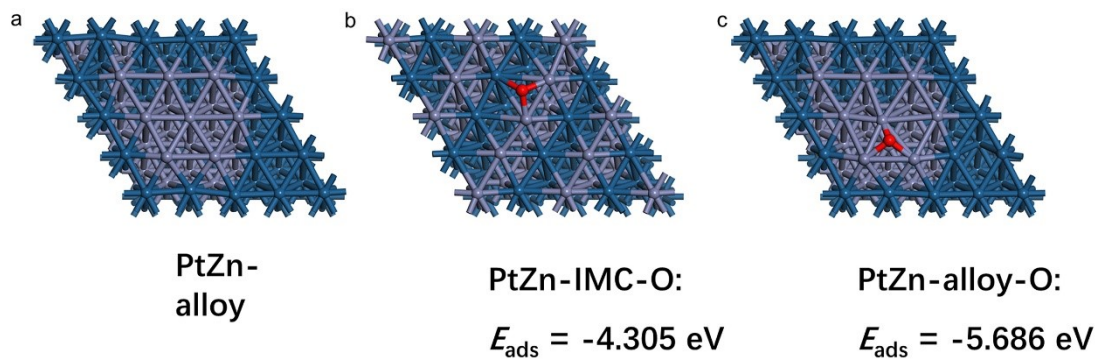


Figure S8. O* Adsorption model and corresponding desorption energy of PtZn alloy and PtZn-IMC.

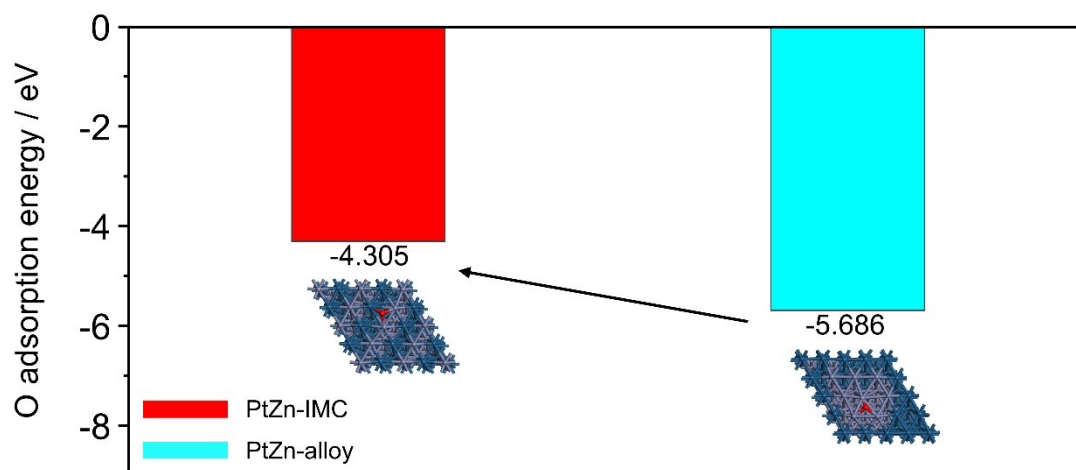


Figure S9. Adsorption free energy of O* intermediate on Pt surface for PtZn alloy (cyan) and PtZn-IMC (red).

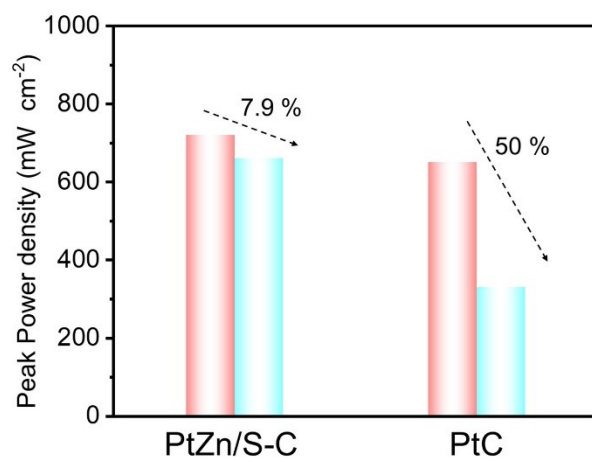


Figure S10. Comparison of peak power density for Pt/C, PtZn/S-C MEA catalyst after 30,000 cycles durability test.

Table S1. ICP-OES results of PtZn-S/C catalysts.

Sample	Pt (wt%)	Zn (wt%)	Pt/Zn
PtZn-S/C-300	19.5	7.6	0.86
PtZn-S/C-600	17.9	6.5	0.92
PtZn-S/C-850	16.7	5.8	0.96

Table S2. Comparison of Particle size and Ordering degree for PtZn/S-C-T catalyst.

	Particle size	Ordering degree
PtZn/S-C-300	2.46 nm	/
PtZn/S-C-600	2.83 nm	/
PtZn/S-C-800	3.05 nm	55.8
PtZn/S-C-850	3.15 nm	80.1
PtZn-C-850	58.27 nm	64.3

Table S3. XPS peak of Pt_{4f} fitting results.

	Area Pt (0)	Area Pt(II)	Pt (0)/ Pt (0) + Pt(II)
300 °C	22833	23936	0.488
600 °C	20272	25267	0.445
850 °C	78849	35688	0.688

Table S4. Comparison of ECSA, MA and SA for Pt/C catalyst after 30, 000 cycles durability test.

Pt/C	ECSA ($\text{m}^2 \text{g}_{\text{Pt}}^{-1}$)	MA ($\text{A mg}_{\text{Pt}}^{-1}$)	SA ($\text{mA cm}_{\text{Pt}}^{-2}$)
initial	66.08	0.25	0.38
30k	28.58	0.08	0.29

Table S5. Comparison of ECSA, MA and SA for PtZn-C catalyst after 30, 000 cycles durability test.

PtZn-C	ECSA ($\text{m}^2 \text{g}_{\text{Pt}}^{-1}$)	MA ($\text{A mg}_{\text{Pt}}^{-1}$)	SA ($\text{mA cm}_{\text{Pt}}^{-2}$)
initial	80.06	1.11	1.39
30k	66.24	0.83	1.26

Table S6. Comparison of ECSA, MA and SA for PtZn/S-C catalyst after 30, 000 cycles durability test.

PtZn/S-C	ECSA ($\text{m}^2 \text{g}_{\text{Pt}}^{-1}$)	MA ($\text{A mg}_{\text{Pt}}^{-1}$)	SA ($\text{mA cm}_{\text{Pt}}^{-2}$)
initial	83.06	1.50	1.81
30k	81.36	1.39	1.71

Table S7. H₂-air polarization performance of PtZn catalyst.

Current density (A/cm ²)	Power density (W/cm ²)	Cell voltage (V)	HFR (mΩ/cm ²)
8.1536E-4	7.5591E-4	0.92811	47.68
0.03812	0.03356	0.88177	47.53
0.07949	0.06593	0.83257	47.54
0.20362	0.15877	0.7865	47.43
0.40433	0.29514	0.7428	47.46
0.6503	0.44228	0.70006	47.43
0.89551	0.56368	0.65618	47.44
1.09491	0.63452	0.61159	47.42
1.24789	0.66104	0.56629	47.46
1.36118	0.65331	0.5202	47.445
1.45741	0.62583	0.47405	47.39
1.53622	0.58311	0.4292	47.35
1.59746	0.52697	0.38614	47.38
1.64617	0.46089	0.34352	47.395

Table S8. H₂-air polarization performance of Pt/C catalyst.

Current density (A/cm ²)	Power density (W/cm ²)	Cell voltage (V)	HFR (mΩ/cm ²)
0	0	0.8625	48.875
0.0096	0.00794	0.82549	48.945
0.03495	0.02734	0.78242	48.82
0.06408	0.04643	0.7306	48.63
0.13345	0.09005	0.68566	48.855
0.24652	0.15385	0.64302	48.715
0.39053	0.22427	0.60277	48.685
0.54144	0.28397	0.56236	48.655
0.67089	0.31845	0.52083	48.555
0.76835	0.32585	0.47594	48.74
0.84464	0.31611	0.42944	48.585
0.91	0.309	0.34	48.745