Supporting Information

B-site W ions doped $La_{0.5}Sr_{0.5}Co_{1-x}W_xO_{3-\delta}$ perovskite nanofibers with

defects as bifunctional oxygen catalysts for rechargeable zinc-air

batteries

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1. Materials

Lanthanum nitrate hexahydrate (La(NO₃)₃·6H₂O, 98%, Guangfu Fine Chemical Research Institute in TianJin), Cobalt nitrate hexahydrate (Co(NO₃)₂ • 6H₂O, AR, 99 %), Ammonium Metatungstate ((NH₄)₆H₂W₁₂O₄₀• *x*H₂O, 99.5 % metal basis) Ruthenium oxide (RuO₂) were chased from Aladdin. trontium acetate ((CH₃CO₂)₂Sr (99 %, Ourchem), PVP (K-90, 98 %, HuaMaiKe) N-N-Diemthylformamide (DMF, 98 %, and Potassium hydroxide (\geq KOH, 85 %) were acquired from FuChen Chemical. Aluminum Oxide Polishing Solution (5 µm, Alliedhightech). Carbon black, acetylene, 50 % compressed, 99.9% was obtained from Alfa Aesar. The commical Pt/C was obtained from Shanghai Hesen Electric Co. Ltd. Deionized water (DIW, 18.2 MΩ) was used for all the catalyst synthesis and electrochemical tests.

2. Material characterizations

The morphologies and structures of the samples were acquired by using the scanning electron microscopy (SEM, Pro, Phenom, Netherlands) and transmission scanning electron microscopy (TEM, JEM-2100 (JEOL, Japan). The X-ray diffraction (XRD, Rigaku Ultima IV, Japan) using a Cu Ka radiation (λ =0.15406 nm) was used to analyst crystallization characteristics. The surface chemical composition and chemical Valence were identified by X-ray photoelectron spectroscopy (XPS, Escalab 250xi. Thermo Fisher Scientific USA). Ultraviolet Photoelectron Spectroscopy (UPS, Escalab 250xi. Thermo Fisher Scientific USA). Brunauer-Emmett-Teller (BET) specific surface area (Quanta chrome ASIQM-0001-3 instrument USA) Inductive Coupled Plasma Optical Emission Spectrometer (ICP-OES, American Agilent 730). The decomposition was obtained by thermal-gravity-analysis (TGA, 449F3-QSM 402D-IS50, Germany).

3. Electrochemical Measurements

The oxygen evolution reaction (OER) activity was measured by the traditional three-electrode system, Hg/HgO (sat. KOH) electrode and graphite rod are used as reference electrode and counter electrode respectively. The catalyst ink was prepared mixing 10 mg catalyst sample add into 0.85 ml DI water ,0.4 ml ethanol and 50 μ L

nafion monomer, the mixed solution was ultrasonic for 20 minutes, Carbon paper was loaded 100 μ L catalyst ink, (loading=1.538 mg/cm²), the CorrTest electrochemical workstation was used to test. Firstly, The four-mouth bottles of 1 M KOH are filled with O₂ (99.9 %) for half an hour, then followed by 50 rounds of CV activation. Next, it was recorded by linear sweep voltammetry (LSV) at a scan rate of 5 mV/s. The stability test was measured by timing current method. Electrical double layer capacitance (*C_{dl}*) was tested at different Cyclic Voltammetry Vitae (CV) scanning speed for 20, 40, 60, 80, 100 mV/s, respectively. The potentials were calculated by the formula:

$E_{\rm RHE} = E_{\rm Hg/HgO} + 0.0592 \rm pH + 0.098 ~ V$

Which E_{RHE} is the potential vs. Reversible hydrogen electrode (RHE), $E_{\text{Hg/HgO}}$ is the potential vs. Hg/HgO electrode, and pH is the PH value of electrode. Preparation of catalyst inks for ORR and Zn-air battery tests. The catalyst sample 5 mg was mixed with carbon black 5 mg and added into 0.85 ml deionized water, 0.4 ml ethanol and 50 μ L Nafion. The mixed solution was ultrasonized for 10min. The oxygen reduction reaction (ORR) activity also measure by traditional three-electrode system, using catalyst coated GC rotating disk electrode (RDE) tip as the working electrode (loading 0.195 mg/cm²), saturated calomel electrode (SCE) (sat. KCl) and graphite rod are used as reference electrode and counter electrode respectively, in the same way, saturated oxygen was passed through in 0.1M KOH. The test using a CHI660E electrochemical workstation, the RDE was swept at 100 mV/s for 50 cycles prior to the ORR test. The LSV was plotted at a scanning rate of 5 mV/s at 1600 rpm, the overpotential and electron transfer number were calculated following the equation:

$$E_{\text{RHE}} = E_{\text{SCE}} + 0.0592 \text{pH} + 0.098 \text{ V}$$

n= 4I_d/(I_d+I_r/N)

4. Zn-Air battery fabrication and testing

The Zn-Air battery were consisted of zinc foil, 6 M KOH and $0.2M Zn(Ac)_2$ electrolyte, Whatman TM Glass microfiber separator and the nickel foam. The prepared catalyst coated on the gas diffusion layer (GDL) were used as cathode (loading 2 mg/cm²). The zinc sheet as the anode. The text was carried out at room

temperature using a CorrTest electrochemical workstation.



Fig. S1. (a-c) SEM image of a series of LCO_3 and $LSCW_x$ (x = 0, 0.1, 0.3 and 0.5) catalysts.



Fig. S2. (a) and (c) N_2 adsorption-desorption isotherms of LCO₃ and LSCW_{0.3}, respectively. (b) and (d) the pore-size distribution curve of LCO₃ and LSCW_{0.3}, respectively.



Fig. S3. (a) TGA curve of $LSCW_{0.3}$ nanofiber.



Fig. S4. XPS spectra of LCO₃, LSC and LSCW_{0.3}, (a) survey spectra and (b) Sr 3d spectra of LSC and LSCW_{0.3}.



Fig. S5. The CV measurements in a non-faradic current region (0.45-0.5 V) *vs.* RHE of (a) LCO₃, (b) LSC, (c) LSCW_{0.1}, (d) LSCW_{0.3}, (e) LSCW_{0.5} and (f) RuO₂ samples at different scan rates of 20, 40, 60, 80, 100, and 120 mV s⁻¹, respectively.

Tab. S1. ICP-OES result of LSCW_{0.3}

element	wt %	element	wt %	element	wt %	element	wt %
Со	19.7784	La	23.3216	Sr	11.1065	W	7.0438

Catalyst	OER (V)	ORR (V)	Limiting current density (mA cm ⁻²)	Ref.
LSCW _{0.3}	1.59	0.58	4.3	This work
$LaCo_{0.8}Ru_{0.2}$	1.69	$E_{i=3}=0.63$	4.4	S 1
$Pt/Sr(Co_{0.8}Fe_{0.2})_{0.95}P_{0.05}O_{3-\delta}$	_	0.81	~6	S2
Ba _{0.6} Sr _{0.4} Co _{0.79} Fe _{0.21} O _{2.67} -NiFe- 25	1.57	_	-	83
S-LCO	1.59	_	4.8	S4
Mg-LaNiO ₃	1.68	0.69	4.2	S5
$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$	1.53	0.73	4.13	S 6
LaCeCoO ₃	1.68	0.72	4.91	S7

Tab. S2. Comparison of OER and ORR activity of reported various perovskite catalysts

Catalyst	Current density (mA cm ⁻²)	Cyclic stability	Power Density (mW cm	V Ref.
LSCW _{0.3}	5	111 h	121.23	This work
LCRO ₈₂	_	240	139	S1
$Pt/Sr(Co_{0.8}Fe_{0.2})_{0.95}P_{0.05}O_{3-\delta}$	5	80	122	S 2
$Ba_{0.6}S_{r0.4}Co_{0.79}Fe_{0.21}O_{2.67}/NiFe25$	5	100 cycles	52.8	S3
S-LCO ₃	2	100 h	92	S4
Mg-doped-LaNiO ₃	10	110 h	45	S5
$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$	10	150 cycles	127	S6
LaCeCoO ₃	5	160 h	60	S7

Tab. S3. Comparison of Zn-air batteries performance with reported various perovskite catalysts

Reference

- S1. M. Wang, B. Han, J. Deng, Y. Jiang, M. Zhou, M. Lucero, Y. Wang, Y. Chen, Z. Yang, A. T. N'Diaye, Q. Wang, Z. J. Xu and Z. Feng, ACS Appl. Mater. Inter, 2019, 11, 5682-5686.
- S2. X. Wang, J. Sunarso, Q. Lu, Z. Zhou, J. Dai, D. Guan, W. Zhou and Z. Shao, Adv. Energy. Mater, 2020, 10, 1903271.
- S3. J. Ran, T. Wang, J. Zhang, Y. Liu, C. Xu, S. Xi and D. Gao, *Chem. Mater*, 2020, **32**, 3439-3446.
- S4. R. Majee, Q. A. Islam and S. Bhattacharyya, ACS Appl. Mater. Inter, 2019, 11, 35853-35862.
- S5. J. Bian, R. Su, Y. Yao, J. Wang, J. Zhou, F. Li, Z. L. Wang and C. Sun, ACS Appl. Mater. Inter, 2019, 2, 923-928.
- S6. Y. Bu, O. Gwon, G. Nam, H. Jang, S. Kim, Q. Zhong, J. Cho and G. Kim, *ACS Nano*, 2017, 11, 11594-11601.
- S7. J. Qian, T. Wang, Z. Zhang, Y. Liu, J. Li and D. Gao, Nano Energy, 2020, 74.