# **Supporting Information**

# Pyrochlore-type Cobalt and Manganese Antimonate Electrocatalysts with Excellent Activity and Stability for OER in Acidic Solution

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# 1. Experimental

#### 1.1 Sample synthesis and characterization

Solid-state reaction was used to synthesize CSO on Ni foam.<sup>1, 2</sup> The degreased Ni foam was immersed in an ultrasonic sonicator for 30 minutes in an organic solvent mixture (acetone: ethanol: deionized water = 1: 1: 1). Additionally, to remove the oxidation layer on the surface of the Ni foam, it was treated with 3 M HCl for 15 minutes and then washed with deionized water. The pretreated Ni foam was dipcoated in the mixtures that acetates (Co(Ac)<sub>2</sub>·4H2O ) and Sb<sub>2</sub>O<sub>5</sub> was ground in anhydrous ethanol for 1 min, and dried under vacuum at 80 °C for 30 min. Then, it was calcined in air at 150 °C and 450 °C for 12 h. The MSO on Ni foam were prepared in the same method.

## 1.2 Electrochemical measurements

Electrochemical measurements were tested using a three-electrode cell with CHI 760E electrochemical workstation (CH Instruments, Inc.). A graphite electrode was used as the counter electrode. In 0.5 M H<sub>2</sub>SO<sub>4</sub> solution, the Hg/Hg<sub>2</sub>SO<sub>4</sub> (saturated K<sub>2</sub>SO<sub>4</sub>, R0401) electrode was selected as reference and converted to the RHE potential using *E* (versus RHE) =*E* (versus Hg/Hg<sub>2</sub>SO<sub>4</sub>) +0.0591×pH+0.658 V. The LSV curves were conducted at a potential sweep rate of 10 mV s<sup>-1</sup> between 1.0 V and 1.8 V (vs. RHE) in acidic condition with O<sub>2</sub> saturation. Electrochemical impedance spectroscopy (EIS) data was tasted at the open circuit potential with a frequency region from 0.01 Hz to 10<sup>6</sup> Hz. The *iR*-compensation was used to correct polarization curves. CSO, MSO, and CO have compensated ohmic resistances of 3.1, 3.7, and 3.2, respectively, measured by EIS in the open circuit voltage. The turnover frequency (TOF) was estimated using the following formula, assuming 100% Faradaic efficiency:

$$TOF = \frac{J \times A}{4 \times F \times n}$$

Where the j (mA cm<sup>-2</sup>) is the measured current density at  $\eta = 250 - 400$  mV, A

 $(0.0706 \text{ cm}^2)$  is the surface area of the glassy carbon RDE, the number 4 means 4 electrons mol<sup>-1</sup> of O<sub>2</sub> in OER reaction, F is Faraday's constant (96485 C mol<sup>-1</sup>), and n is the moles of coated metal atom on the electrode calculated from catalysts.<sup>3</sup>

## 1.3 Density function theory calculation

The calculations were performed in the framework of density functional theory (DFT) with the projected augmented wave (PAW) method<sup>4</sup>, using the Vienna ab initio simulation package (VASP)<sup>5</sup>. For geometry optimization and energy calculation, in consideration of computation cost, PBE-GGA+U method was applied to treat the exchange-correlation energy<sup>6</sup>. The addition of the Hubbard U term can partially avoid the incorrect description of the strong electron correlation in Co 3d orbital. When employing the GGA+U approach, a key step is the choice of U value. In this work, U was set to 3.3 eV for Co-3d<sup>7</sup>, which was fitted to reproduce the lattice parameters of Co<sub>3</sub>O<sub>4</sub>. The calculated band gap is 0.72 eV, still lower than the observed value of 1.86 eV in our experiment. To further correct the error in band gap caused by GGA, the HSE06 hybrid functional<sup>8</sup> were applied to achieve more accurate electronic structure of CSO, and Co3O4. In HSE, the fraction of exact exchange in a Hartree-Fock/DFT hybrid functional was set to 0.25, which could achieve 2.03 eV in band gap of CSO. In addition, the plane-wave energy cutoff was set to 450 eV, and the  $\Gamma$ -point centered 5×5×5 and 3×3×3 k-point mesh were used for GGA+U and HSE, respectively. The calculated and experimental crystal structural data from bulk CSO is illustrated in Table S1, along with data from other experiment. Obviously, the calculated results give good agreement with the experiment ones, meaning the setting for GGA+U and HSE in the calculation is reliable. Besides, the calculated data processing tasks were based on VESTA<sup>9</sup>, Bader<sup>10</sup> and vaspkit software package<sup>11</sup>.



Fig. S1. The binding energy of CSO, MSO and CO mersured by UPS.

The work function ( $\phi$ ) were determined by the difference between the photo energy (21.2 eV) and the binding energy. The CSO (4.85 eV) shows the lowest work function amount the MSO (5.90 eV) and CO (6.82 eV).



Fig. S2. (a) The TOF plots at different overpotentials in 0.5 M  $H_2SO_4$ . (b) The measured metals concentration in electrolyte by ICP over the course of the CP measurements.

Element	Weight percentage %	Atomic percentage %
ОК	18.56	56.34
Co K	26.26	21.65
Sb L	55.18	22.01
Total account	100	100

Table S1. The element content of CSO.

	M(Co <sub>2</sub> Sb <sub>2</sub> O <sub>7</sub> )/	$m(C_{0}, Sh, O)/ma$	$V(N_{0} \in \Omega)/m$	s
	g mol <sup>-1</sup>	$III(C0_2SD_2O_7)/IIIg$	v (1\a <sub>2</sub> S <sub>2</sub> O <sub>4</sub> )/1111	0
1	473.38	50	3.65	
2	473.38	50	3.35	1.02
3	473.38	50	3.05	1.02
4	473.38	50	3.30	

Table S2. The results of oxygen vacancy proportion by iodometry.

Catalyst	Electrolytes	Activity	Stability	Ref.
	$\mathbf{Co_2Sb_2O_7}$ 0.5 M H <sub>2</sub> SO <sub>4</sub>	288 mV	40 h	This
$Co_2Sb_2O_7$		@ 10 mA cm <sup>-2</sup>	@ 1 mA cm <sup>-2</sup>	work
		~760 mV	24 h	12
	$0.5 \text{ M H}_2 \text{SO}_4$	@ 10 mA cm <sup>-2</sup>	@ 10 mA cm <sup>-2</sup>	12
		~672 mV	12 h	13
C0 <sub>3</sub> O <sub>4</sub> /F1O	$0.5 \text{ M H}_2 \text{SO}_4$	@ 10 mA cm <sup>-2</sup>	@ 10 mA cm <sup>-2</sup>	15
			2000 CV cycles	
Ag-doped		470 mV	between	14
C0 <sub>3</sub> O <sub>4</sub>	$0.5 \text{ M H}_2 \text{SO}_4$	@ 10 mA cm <sup>-2</sup>	1.66 and 1.76	14
			V <sub>RHE</sub>	
D.O	$0.5 \text{ M H}_2 \text{SO}_4 +$	367 mV		15
RuO <sub>2</sub>	1.33 M Na <sub>3</sub> SO <sub>4</sub>	@ 1 mA cm <sup>-2</sup>	-	15
		~190 mV	የኬ	
Y <sub>2</sub> Ru <sub>2</sub> O <sub>7</sub>	0.1 M HClO <sub>4</sub>	@ onset	8 fl @ 1 mA cm <sup>-2</sup>	16
		overpotential		
V.Ir.O.	0.1 M HC10.	0.86 mA cm <sup>-2</sup>	24 h	17
1 211 207	0.1 WI HCIO <sub>4</sub>	@1.50V	@ 1 mA cm <sup>-2</sup>	
Ph. Ir. /VXC	0.5 M H.SO.	292 mV	8 h	18
<b>KII221178/ V AC</b>	$0.5 \text{ WI } 11_2 \text{ SO}_4$	@ 10 mA cm <sup>-2</sup>	@1.53 V <sub>RHE</sub>	
ՇօԸս.℞ս.Օ.,	0.5 M H.SO.	273 mV	100 CV cycles	19
	0.5 WI 112504	@ 1 mA cm <sup>-2</sup>	100 C V Cycles	
Fe-Si-	50 c/L H SO	735 mV	1000 CV eveles	20
F 05513	50 g/L 11 <sub>2</sub> 504	@ 10 mA cm <sup>-2</sup>	1000 CV Cycles	
Mng .O. Bre	0.5 M H-SO	295 mV	500 h	21
$\mathbf{Mn}_{7.5}\mathbf{O}_{10}\mathbf{Br}_{3}$	$0.5 \text{ M H}_2 \text{SO}_4$	@ 10 mA cm <sup>-2</sup>	500 11	

 Table S3. Summary of OER performance for some representative recently-developed
 electrocatalysts in acidic solution.

Catalysts	Element	Concentration for metal ion/mg L <sup>-1</sup>
CSO	Со	0.30
CSU	Sb	0.34
MSO	Mn	0.68
MSU	Sb	0.68
СО	Со	0.80

Table S4. ICP analysis of metal ions concentration after CP test in 0.5 M  $H_2SO_4$ .

	$M_2S$	$b_2O_7$
	M = Co	M = Mn
<i>a</i> (Å)	10.159	10.281
Sb-O`(Å)	1.98	1.99
M-O` (Å)	2.48	2.53
M-O`` (Å)	2.20	2.23
$\angle$ M-O`-M (deg.)	92.84	91.62
∠O``-M-O` (deg.)	78.84	79.46
x	0.332	0.328
Band gap (eV)	0.72 (GGA+U) 2.03(HSE)	0.00(GGA+U) 1.115(HSE)

Table S5 Calculated lattice parameters and band gap of CSO and MSO.

	$Co_2Sb_2O_7$	$Mn_2Sb_2O_7$
Vo	0.771	2.605
V <sub>O</sub> -V <sub>M</sub>	-0.485	1.007

Table S6. Formation energy (eV) of V<sub>O</sub> and V<sub>O</sub>-V<sub>M</sub> complex in MSO

The formation energy  $E^{\rm f}$  of V<sub>0</sub> and V<sub>0</sub>-V<sub>M</sub> complex (M=Co or Mn) can be defined as

$$E_{V_0} F_{V_0} = E_{V_0} F_{M} + E_{M0} - E_{M_2 S b_2 O_7}$$
(1-1)

$$E_{V_0}^{f} = E_{V_0} + \frac{1}{2}E_{0_2} - E_{M_2Sb_2O_7}$$
(1-2)

where  $E_{M2Sb2O7}$  is the total energy of the supercell MSO.  $E_{Vo}$  and  $E_{Vo-VM}$  are the total energy of the supercell with V<sub>0</sub> and V<sub>0</sub>-V<sub>M</sub>, respectively.  $E_{O2}$  and  $E_{MO}$  are the total energy of a unit O<sub>2</sub> and MO, respectively. As shown in Table S6, for CSO, the formation energy of V<sub>0</sub> and V<sub>0</sub>-V<sub>C0</sub> is positive and negative, respectively. It means that single V<sub>0</sub> is not stable in CSO. V<sub>0</sub> exists in the form of V<sub>0</sub>-V<sub>C0</sub> complex, which can maintain the charge neutrality and lower the formation energy. For MSO, the formation of V<sub>0</sub> and its complex is impossible.

	Co <sub>2</sub> Sb <sub>2</sub> O <sub>7</sub>	$Co_2Sb_2O_7-(V_{Co}+V_o)$	C0 <sub>3</sub> O <sub>4</sub>	Mn <sub>2</sub> Sb <sub>2</sub> O <sub>7</sub>
E <sub>Co-3d</sub>	-2.87	-3.23	-2.57	-2.80
ЕО``-2р	-1.35	-1.65	-	-1.97
E <sub>O-2p</sub>	-	-	-3.84	-
EUHB	4.90	4.51	4.55	6.05
$\Delta_{\rm CTE}$	6.25	6.16	8.39	8.02

Table S7. Calculated band centers and CTE of CSO, MSO, CO and CSO-

(17)	- 1 <sup>1</sup>	<b>X</b> 7	)
$(V_{C})$	$b^+$	V <sub>c</sub>	, <b>)</b> .

	$CSO-(V_{Co}+V_o).$	
	$Co_2Sb_2O_7$	$Co_2Sb_2O_7-(V_{Co}+V_o)$
Со	0.583(+2)	0.594(+2)
0`	-0.789(-2)	-0.795(-2)
0``	0.722(-2)	0.741(-2)

Table S8. Computed average Bader charges of Co and O atoms in CSO and

The average Bader charge of the Co atom differs by more than 25% from its theoretical ionic charge of +2, suggesting that the Co-O bond exhibits a strong covalency.

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