Electronic Supplementary Information

Catalytic activity atlas of ternary Co-Fe-V metal oxides for oxygen evolution reaction

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Table S1. Amount of Co, Fe and V precursor used for synthesising different CoFeV PBA precursors.

Sample No.	Designed composition			Precursor volume, mL					
	Co	Fe	V	$CoCl_2$ (50 mM)	$FeCl_2$ (50 mM)	$VOSO_4$ (50 mM)	H_2O	$K_3[Fe(CN)_6]$ (20 mM)	$K_3[Co(CN)_6]$ (20 mM)
1	2	6	2	10	10	10	20	50	0
2	1	6	3	5	10	15	20	50	0
3	3.33	5	1.67	16.65	5	8.35	20	50	0
4	1.67	5	3.33	8.35	5	16.65	20	50	0
5	1	5	4	5	5	20	20	50	0
6	4.5	4	1.5	22.5	0	7.5	20	50	0
7	4	4	2	20	0	10	20	50	0
8	3	4	3	15	0	15	20	50	0
9	2	4	4	10	0	20	20	50	0
10	1.5	4	4.5	7.5	0	22.5	20	50	0
11	1	4	5	5	0	25	20	50	0
12	5	3	2	20	0	10	20	37.5	12.5
13	4.67	3	2.33	18.35	0	11.65	20	37.5	12.5
14	3.5	3	3.5	12.5	0	17.5	20	37.5	12.5
15	6	2	2	10	10	10	20	0	50
16	5.33	2	2.67	16.65	0	13.35	20	25	25
17	2.67	2	5.33	3.35	0	26.65	20	25	25
18	0	10	0	0	30	0	20	50	0
19	0	8	2	0	20	10	20	50	0
20	0	7	3	0	15	15	20	50	0
21	0	5	5	0	5	25	20	50	0
22	0	4	6	0	0	30	20	50	0
23	2	8	0	10	20	0	20	50	0
24	4	6	0	0	30	0	20	0	50
25	6	4	0	30	0	0	20	50	0
26	8	2	0	30	0	0	20	25	25
27	10	0	0	30	0	0	20	0	50
28	8	0	2	20	0	10	20	0	50
29	5	0	5	5	0	25	20	0	50
30	4	0	6	0	0	30	20	0	50

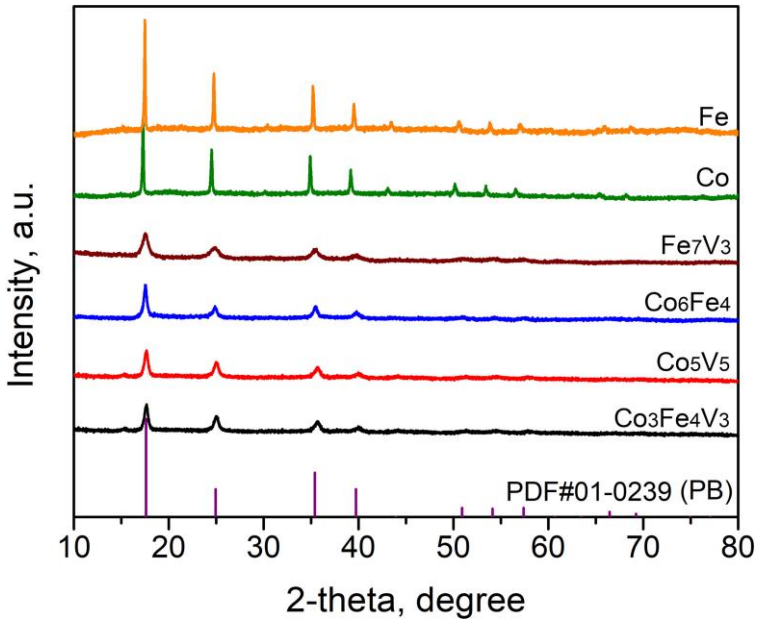

Fig. S1 XRD patterns of different PBA nanoparticles synthesized in this study.

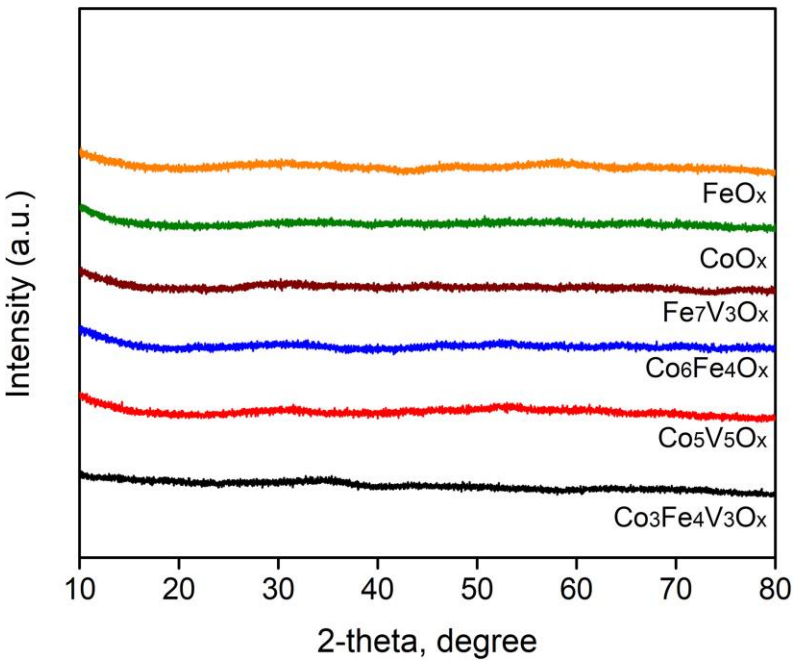

Fig. S2 XRD patterns of metal oxides synthesized in this study.

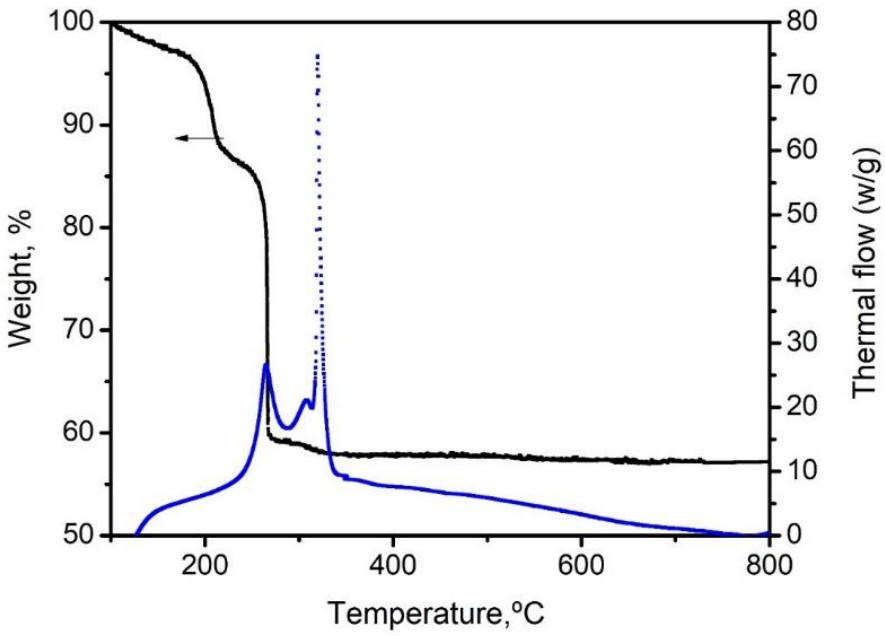

Fig. S3 TGA and thermal flow profile of $Co_3Fe_4V_3$ PBA nanoparticles.

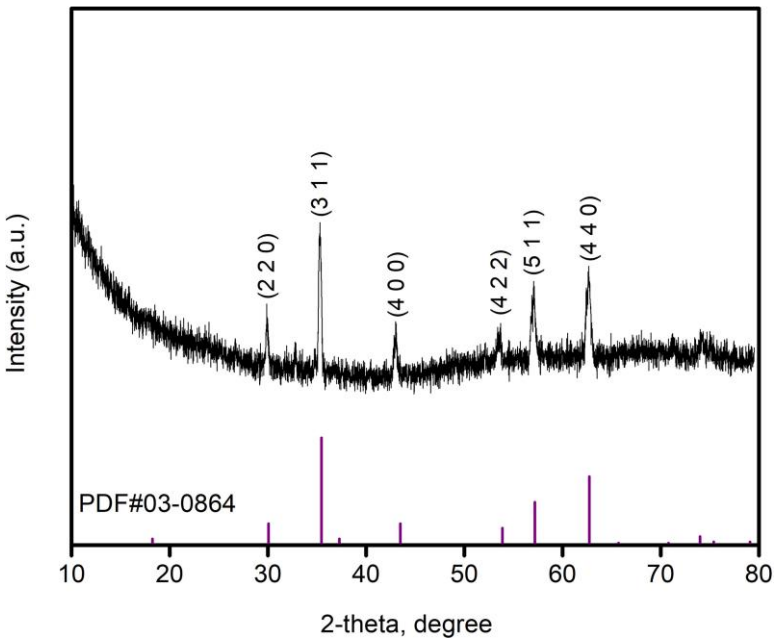

Fig. S4 XRD patterns of $Co_3Fe_4V_3O_x$ nanoparticles obtained after thermally decomposing PBA nanoparticles in the air at 350 ºC. Standard lines of a spinel $CoFe_2O_4$ (PDF#03-0864) is displayed for comparison.

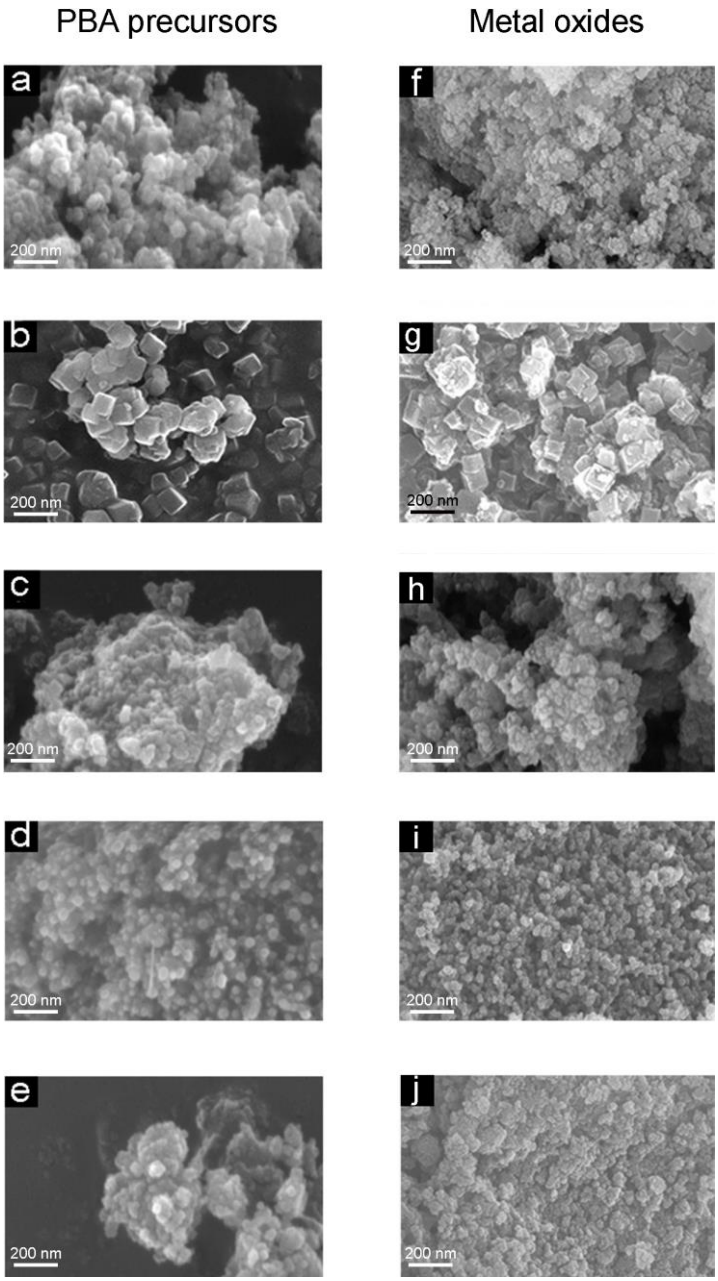

Fig. S5 SEM images of various PBA nanoparticles and their corresponding metal oxide nanoparticles. (a) and (f) Co_6V_4, (b) and (g) Co, (c) and (h) Fe_7V_3, (d) and (i) Co_6Fe_4, (e) and (j) Fe.

Table S2. Particle size of various PBA precursors and their derived metal oxide particles determined by SEM

	Diameter of PBA precursor, nm	Diameter of metal oxide, nm
$Co_3Fe_4V_3$	53.91 ± 4.35	49.57 ± 7.26
Co_6V_4	65.78 ± 5.43	60.05 ± 9.19
Co	96.53 ± 10.93	87.20 ± 7.92
Fe_7V_3	69.38 ± 6.92	53.20 ± 6.09
Co_6Fe_4	51.50 ± 4.87	49.43 ± 5.40
Fe	62.16 ± 9.47	60.38 ± 6.48

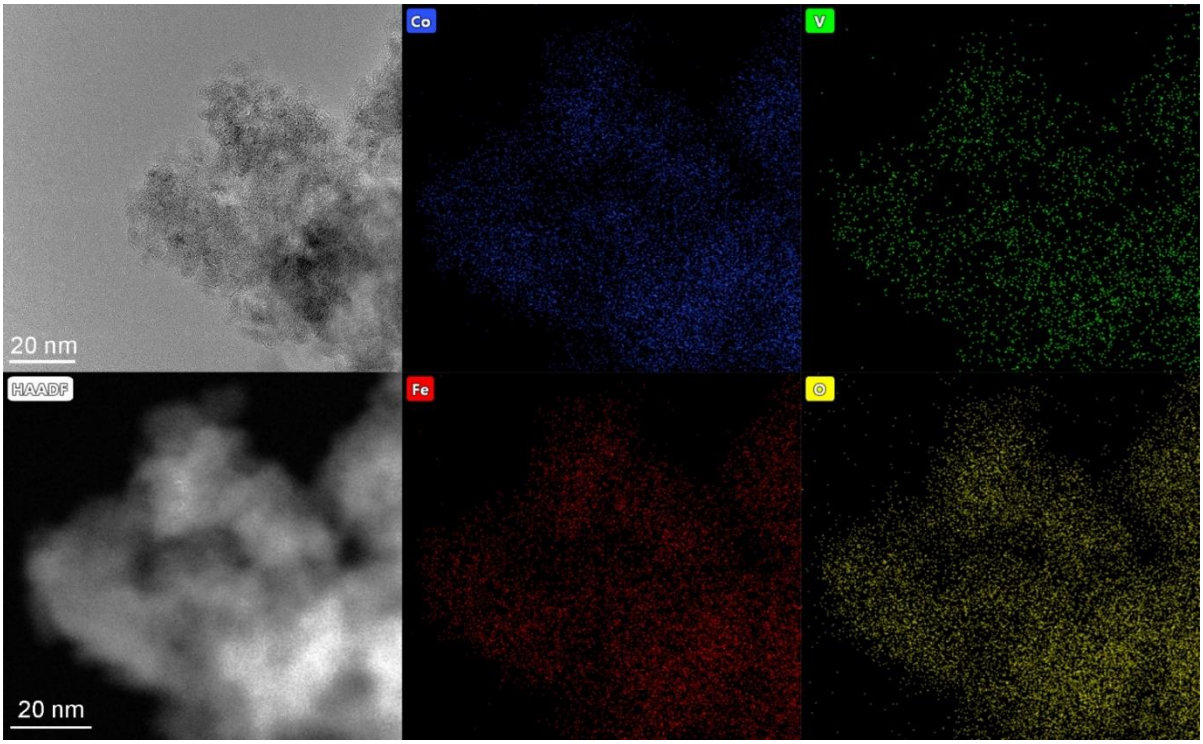

Fig. S6 TEM and HAADF-STEM EDX elemental mappings of $Co_3Fe_4V_3$ PBA nanoparticles.

Table S3. Elemental compositions (in molar ratio) of Co-Fe-V metal oxides determined by different methods.

	Designed			EDX			ICP-AES			XPS		
	Co	Fe	V	Co	Fe	V	Co	Fe	V	Co	Fe	V
$Co_3Fe_4V_3O_x$	3	4	3	2.90	3.99	3.11	2.97	4.09	3.04	2.85	3.96	3.19
$Co_5V_5O_x$	5	0	5	5.03	0.00	4.97	5.11	0.00	4.89	5.16	0.00	4.84
$Co_6Fe_4O_x$	6	4	0	5.93	4.07	0.00	5.88	4.12	0.00	6.06	3.95	0.00
$Fe_7V_3O_x$	0	7	3	0.00	2.89	7.11	0.00	7.07	2.93	0.00	6.95	3.05

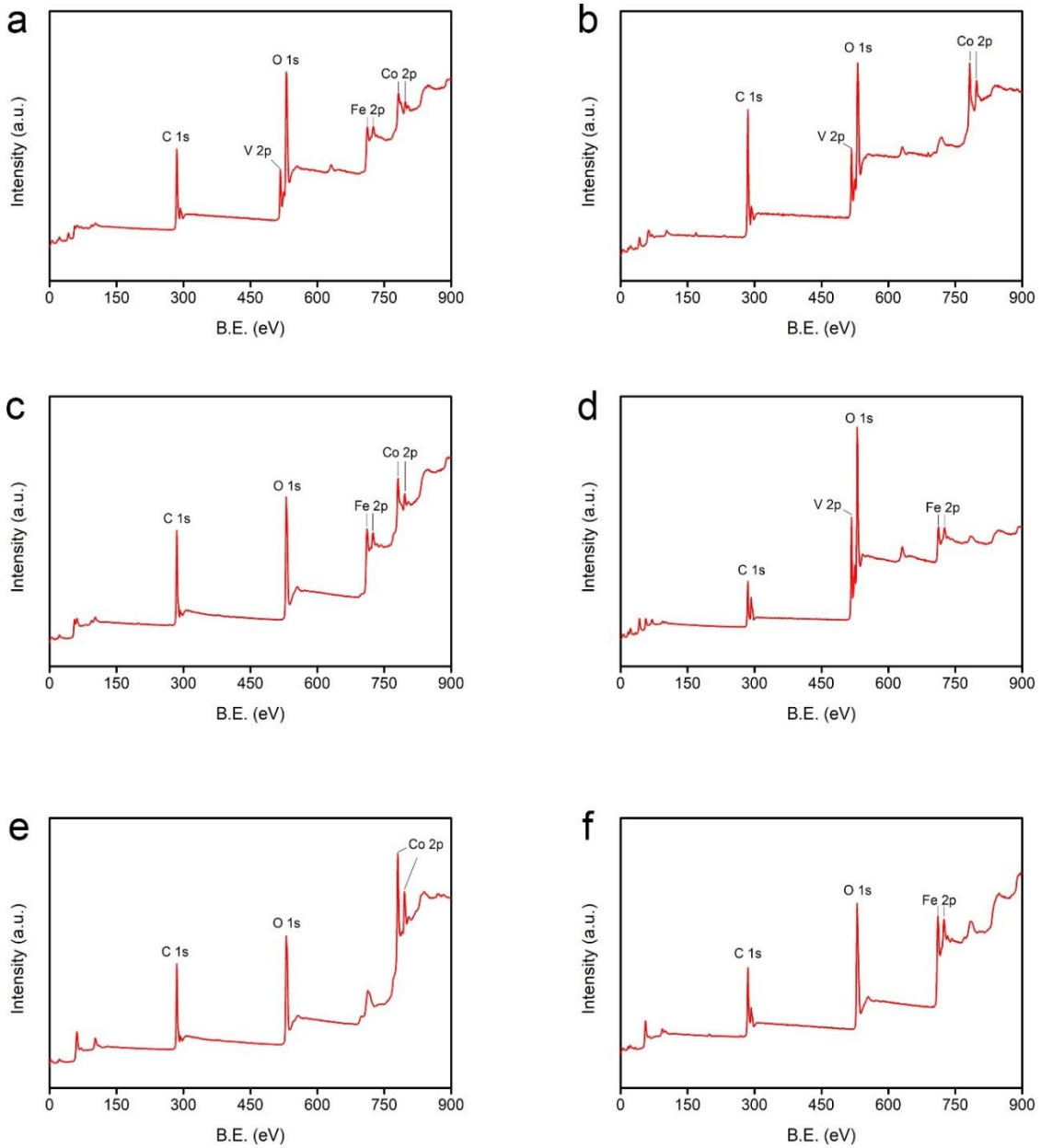

Fig. S7 XPS survey spectra of (a) $Co_3Fe_4V_3O_x$, (b) $Co_5V_5O_x$, (c) $Co_6Fe_4O_x$, (d) $Fe_7V_3O_x$, (e) CoO_x, and (f) FeO_x samples.

Table S4. OER performance of Co-Fe-V metal oxide samples tested in this study.

Sample No.	Designed composition (molar ratio)			Experimental composition (molar ratio) [a]				η_{10}, mV	Tafel slope, mV dec^{-1}
	Co	Fe	V	Co	Fe	V	O [b]		
1	2	6	2	1.94	5.95	2.11	14.71	396	70
2	1	6	3	0.94	6.08	2.98	14.91	419	80
3	3.33	5	1.67	3.09	4.97	1.94	14.23	335	68
4	1.67	5	3.33	1.50	4.97	3.53	15.01	398	67
5	1	5	4	0.94	5.04	4.02	15.13	412	67
6	4.5	4	1.5	4.57	4.08	1.36	13.78	334	74
7	4	4	2	3.78	3.96	2.26	13.60	343	60
8	3	4	3	2.85	3.96	3.19	14.43	249	41
9	2	4	4	1.87	4.07	4.06	15.38	279	63
10	1.5	4	4.5	1.60	4.11	4.29	16.01	292	66
11	1	4	5	0.90	3.95	5.15	16.56	385	74
12	5	3	2	4.89	3.03	2.09	14.13	345	55
13	4.67	3	2.33	4.54	3.07	2.39	13.79	296	47
14	3.5	3	3.5	3.22	2.95	3.82	14.73	287	51
15	6	2	2	5.90	1.93	2.17	14.31	342	62
16	5.33	2	2.67	5.46	1.96	2.58	14.92	313	59
17	2.67	2	5.33	2.82	1.86	5.32	16.31	335	72
18	0	10	0	0.00	10	0.00	14.59	656	153
19	0	8	2	0.00	8.15	1.85	14.74	567	112
20	0	7	3	0.00	6.95	3.05	14.58	519	78
21	0	5	5	0.00	5.10	4.90	16.16	531	87
22	0	4	6	0.00	4.11	5.89	15.99	589	105
23	2	8	0	2.06	7.94	0.00	15.19	458	97
24	4	6	0	4.09	5.91	0.00	14.69	412	71
25	6	4	0	6.06	3.95	0.00	15.13	345	63
26	8	2	0	8.11	1.89	0.00	14.25	372	70
27	10	0	0	10	0.00	0.00	14.59	386	77
28	8	0	2	7.83	0.00	2.17	15.41	369	65
29	5	0	5	5.16	0.00	4.84	15.23	319	56
30	4	0	6	3.87	0.00	6.13	15.85	359	78

a. Determined by ICP-AES measurements.

b. Determined from XPS survey scan. This value is also the x value in different $Co_aFe_bV_cO_x$ samples.

Table S5. Performance comparison of recently reported OER electrocatalysts based on Co, Fe and V oxides.

Sample	Substrate	Electrolyte	η_{10}, mV	Tafel slope, mV dec^{-1}	Ref.
$Co_3Fe_4V_3O_x$	GCE	1 M KOH	249	41	This work
$CoV_{1.5}Fe_{0.5}O_4$	GCE	1 M KOH	300	38	*ACS Catal.*, **2018**, 8, 1259
V-Co-Fe-343(souce)	GCE	1 M KOH	307	36	*J. Mater. Chem. A*, **2015**, 3, 17763
a-$CoVO_x$	GCE	1M KOH	347	51	*ACS Catal.*, **2018**, 8, 644
CoO_x+ Fe^{3+}	GCE	1M KOH	309	27.6	*ACS Catal.*, **2017**, 8, 807
$Fe_{0.5}V_{0.5}OOH$	GCE	1M KOH	390	36.7	*Angew. Chem. Int. Ed.*, **2017**, 56, 3289
VOOH-3Fe	GCE	1M KOH	195	55	*Small*, **2019**, *15*, 1904688
Co_3O_4/Co-Fe Oxide	GCE	1M KOH	297	61	*Adv. Mater.* **2018**, *30*, 1801211
α-$Co_4Fe(OH)_x$	GCE	1M KOH	295	52	*J. Mater. Chem. A*, **2017**, 5, 1078
Co/Fe 15	GCE	0.1M KOH	390	61	*J. Mater. Chem. A*, **2017**, 5, 6849
CoFe35 LDH	GCE	0.1M KOH	350	49	*ChemSusChem*, **2017**, 10, 156
Fe1Co1-ONS	GCE	1M KOH	308	36.8	*Adv. Mater.*, **2017**, 29, 1606793
CoFe2O4	GCE	1M KOH	266	53	*Appl. Catal. B*, **2019**, 245, 1
WCoFex-CNF	Ni Foam	1M KOH	254	44.8	*Small*, **2019**, 15, 1901940
CoFe-H	Graphite	1M KOH	280	28	*Adv. Funct. Mater.*, **2017**, 27, 1603904
Co-Fe	Carbon paper	1M KOH	330	37	*Electrochimi Acta*, **2018**, 260, 872
CoFe	Carbon paper	1M KOH	283	51	*Nano Energy*, **2017**, 53, 576
CoFeV LDH/NF	Ni Foam	1 M KOH	242	57	*ACS Sustain. Chem. Eng.*, **2019**, 7 16828
$Co_{0.8}V_{0.2}OOH$	Ni foam	1M KOH	190	39.6	*J. Mater. Chem. A*, **2019**, 7 21911
CoV-UAH	Au foam	1M KOH	215	-	*Energy Environ. Sci.*, **2018**, 11 1736
Fe-Co_3O_4H-NSs/NF	Ni foam	1M KOH	204	38	*Nano Energy*, **2018**, 54, 238
CoFe/NF	Ni foam	1M KOH	220	40	*Small*, **2018**, 14, 1702568
FCCH/NF	Ni foam	1M KOH	228		*Adv. Energy Mater.* **2018**, 8, 1800175
CoFe PBA-2h	Ni foam	1M KOH	274	53	*Adv. Energy Mater.* **2018**, 8, 1800085

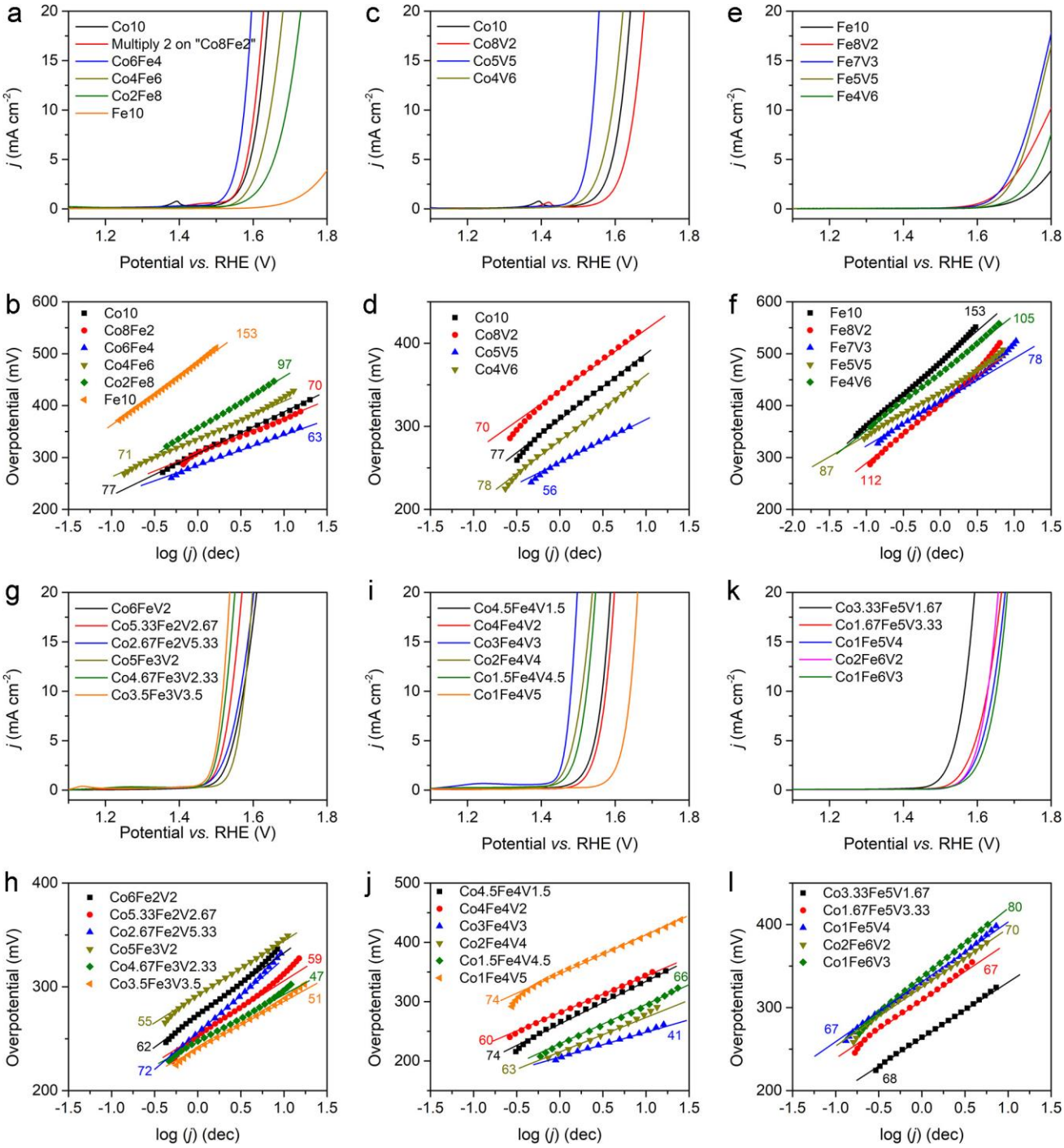

Fig. S8 OER LSV and Tafel plots of tested $Co_aFe_bV_cO_x$ samples. (a) & (b) Co-Fe samples; (c) & (d) Co-V samples; (e) & (f) Fe-V samples; (g) & (h) $Co_aFe_2V_cO_x$ and $Co_aFe_3V_cO_x$ samples; (i) & (j) $Co_aFe_4V_cO_x$ samples (k) & (l) $Co_aFe_5V_cO_x$ and $Co_aFe_6V_cO_x$ samples.

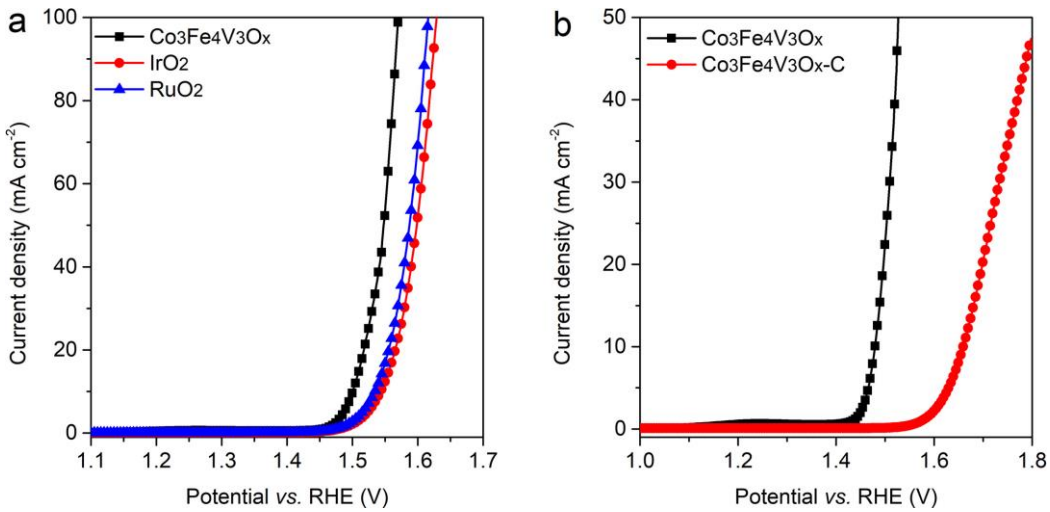

Fig. S9 LSV curves of $Co_3Fe_4V_3O_x$ in comparison to (a) IrO_2 and RuO_2 benchmarks and (b) phase-segregated $Co_3Fe_4V_3O_x$-C sample.

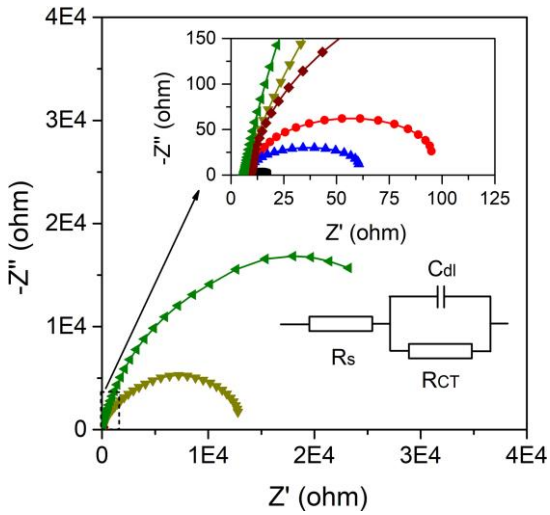

Fig. S10 Full ESI Nyquist plots of different samples and the equivalent circuit.

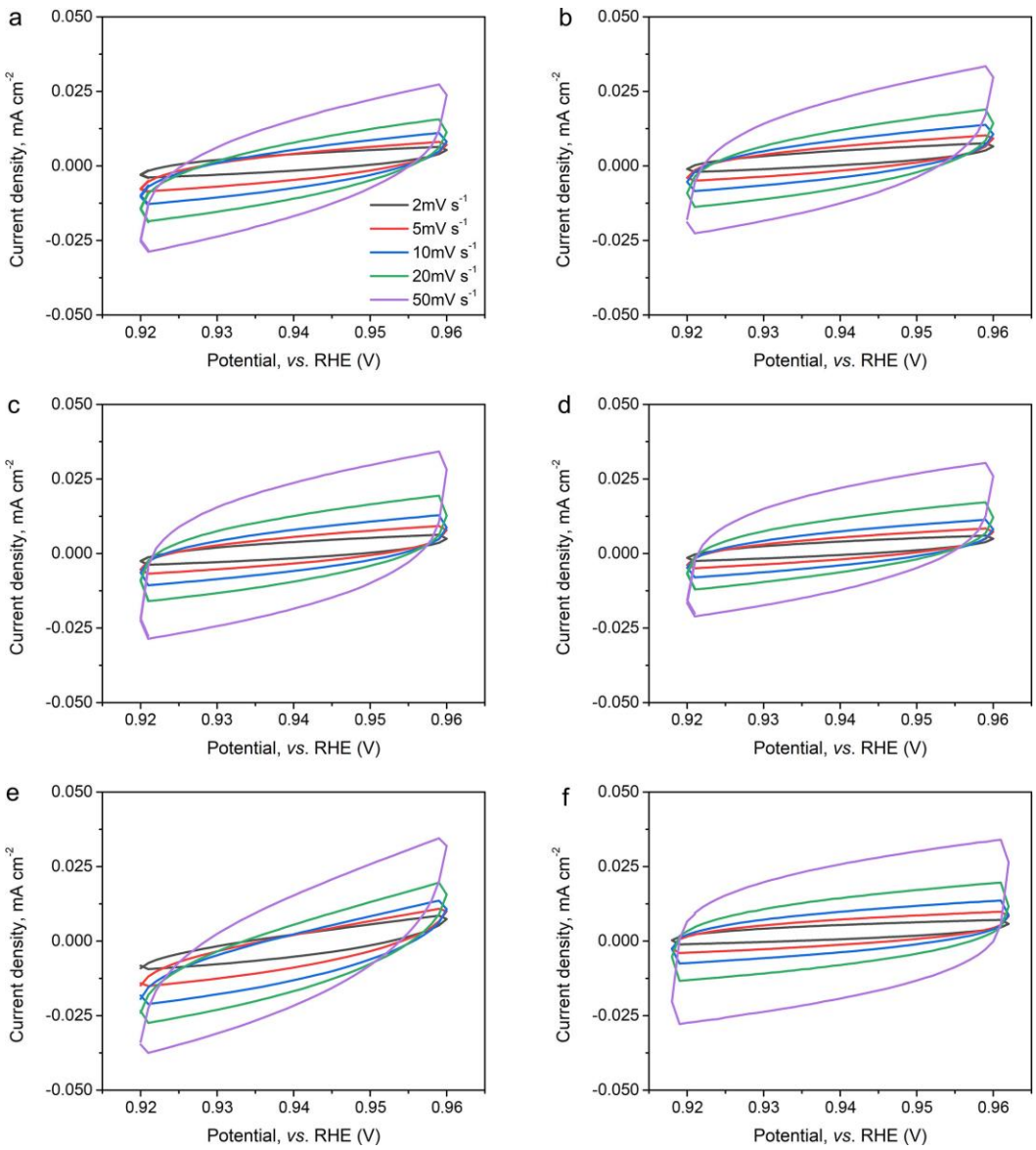

Fig. S11 CV curves of (a) $Co_3Fe_4V_3O_x$, (b) $Co_5V_5O_x$, (c) $Co_4Fe_6O_x$, (d) $Fe_7V_3O_x$, (e) CoO_x, and (f) FeO_x samples collected at different scan rates.

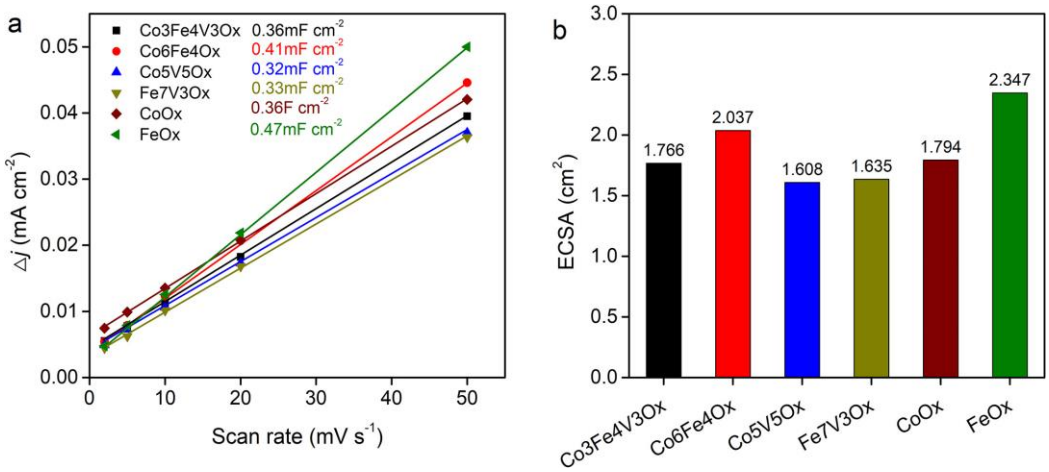

Fig. S12 (a) Δj (0.94 V *vs.* RHE) plotted against scan rate and the calculated C_{dl} and (b) calculated ECSA of different Co-Fe-V metal oxide samples.

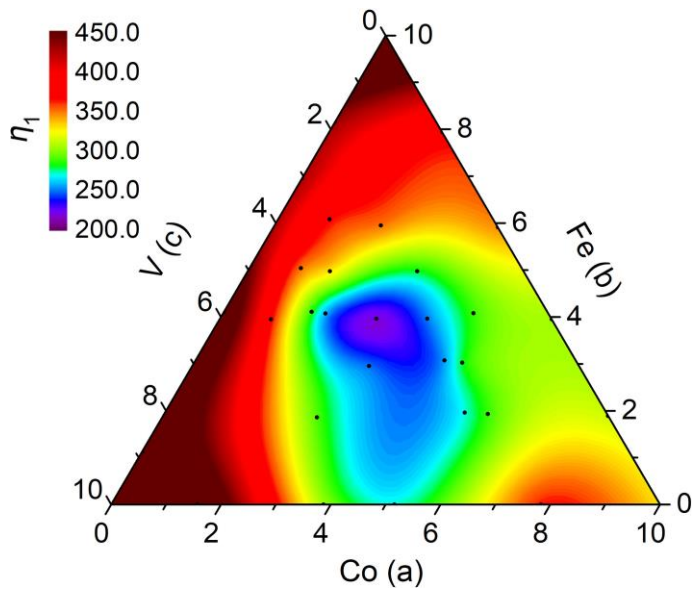

Fig. S13 OER performance atlas of ternary $Co_aFe_bV_cO_x$ based on the overpotential required to reach a j_{ECSA} of 1 mA cm^{-2}. Sample compositions were determinged by ICP-AES and makred by black dots.

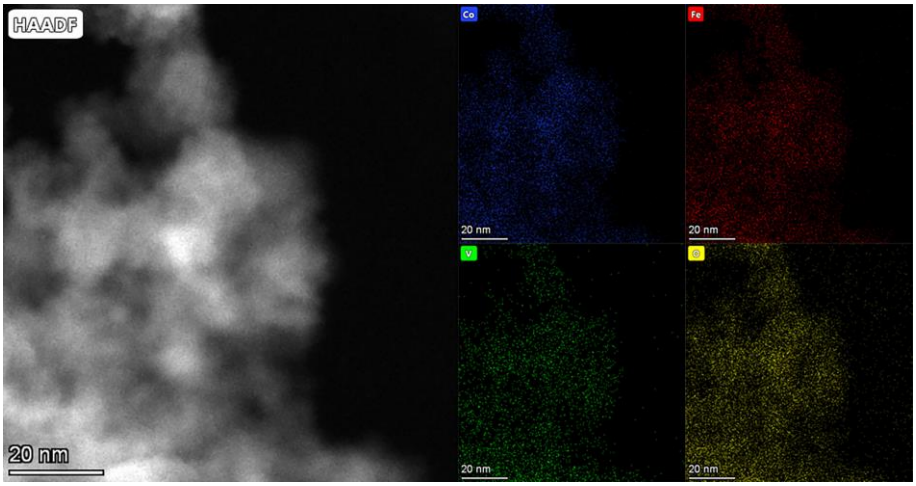

Fig. S14 A TEM image of $Co_3Fe_4V_3O_x$ after the 72-hour OER stability test (left) and the corresponding EDX elemental mappings of Co, Fe, V, and O (right).

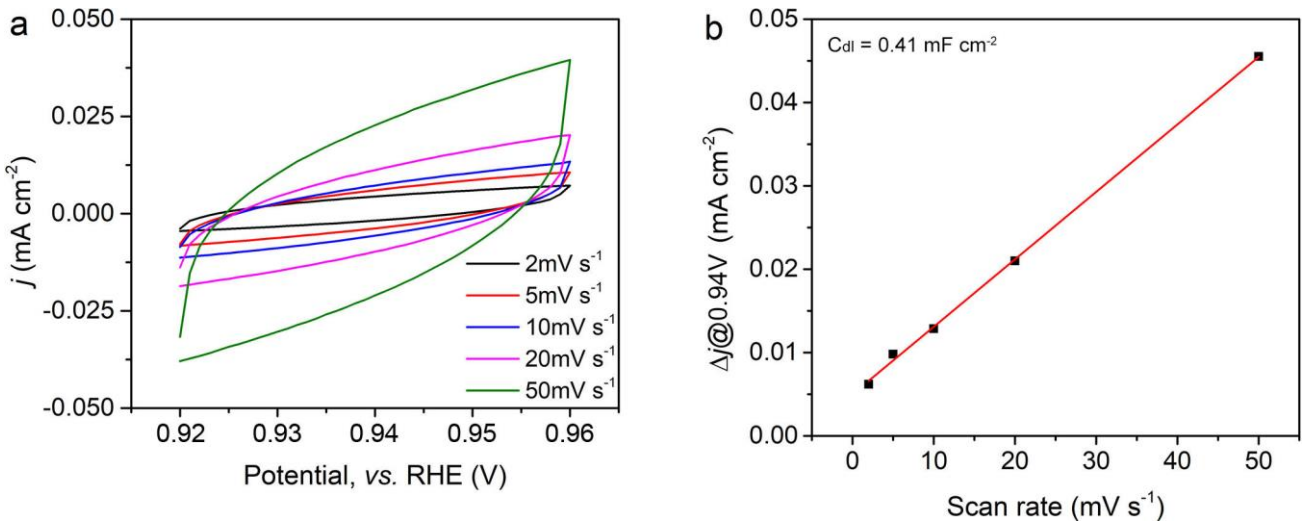

Fig. S15 (a) CV curves obtained at different scan rates and (b) Δj@0.94V plotted against scan rates of the $Co_3Fe_4V_3O_x$ after the OER stability test.

Table S6. Theoretical and experimental onset potential of different samples.

Catalyst	Onset overpotential (V)	
	Theoretical values	Experimental values ($\eta_{ECSA-0.25}$)
Co-CoFeV (near Fe)	0.63	0.19
Co-CoFeV (near V)	1.12	
Co-CoV	0.77	0.28
Co-CoFe	0.87	0.29
Co	0.94	0.35

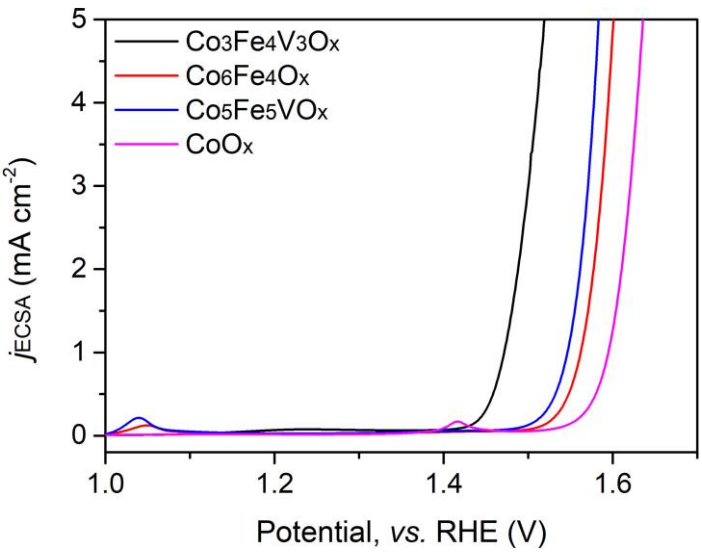

Fig. S16 ECSA normalized LSV curves of different samples.

Table S7. Metal valence contents (at%) in different $Co_aFe_bV_cO_x$ determined from their high-resolution XPS spectra.

	Co^{2+}	**Co^{3+}**		**Fe^{2+}**	**Fe^{3+}**		**V^{3+}**	**V^{4+}**	**V^{5+}**	
Position, eV	781.9	779.9		710.2	711.2		515.6	516.7	517.8	
Catalyst	**Co^{2+}**	**Co^{3+}**	**Co average valence**	**Fe^{2+}**	**Fe^{3+}**	**Fe average valence**	**V^{3+}**	**V^{4+}**	**V^{5+}**	**V average valence**
$Co_3Fe_4V_3O_x$	**73.9**	**26.1**	**2.261**	**18.7**	**81.3**	**2.813**	**13.2**	**62.3**	**24.5**	**4.114**
$Co_5Fe_4V_1O_x$	47.6	52.4	2.524	22.0	78.0	2.780	4.7	73.2	22.1	4.174
$Co_1Fe_4V_5O_x$	77.7	22.3	2.223	14.1	85.9	2.859	10.4	84.7	5.0	3.946
$Co_6Fe_4O_x$	48.6	51.4	2.514	24.2	75.8	2.758	-	-	-	-
$Co_5V_5O_x$	89.6	10.4	2.104	-	-	-	4.1	69.4	26.5	4.224
$Fe_7V_3O_x$	-	-	-	3.4	96.6	2.966	15.4	76.5	8.0	3.926
CoO_x	41.3	58.7	2.587	-	-	-	-	-	-	-
FeO_x	-	-	-	25.8	74.2	2.742	-	-	-	-

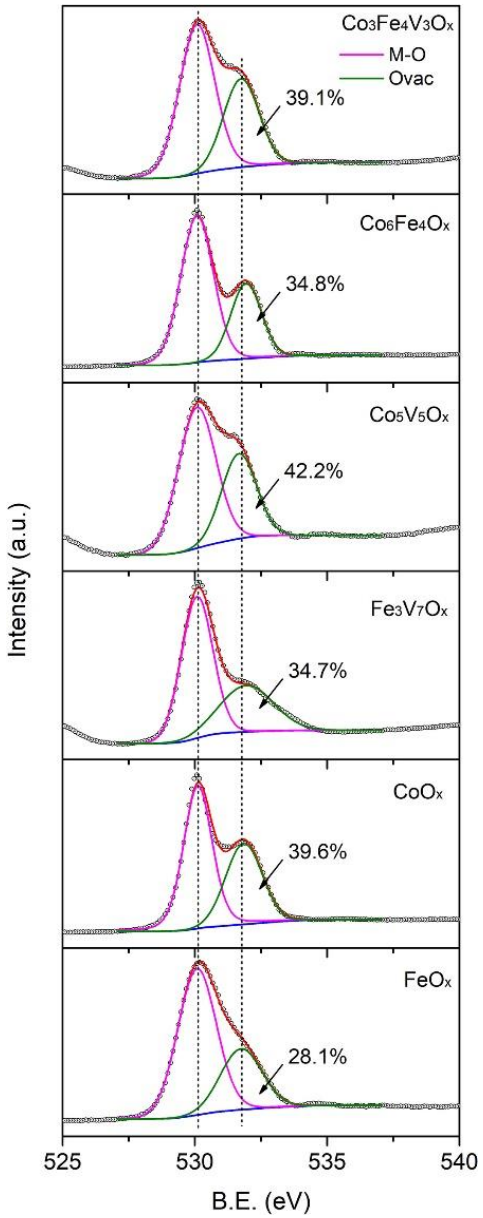

Fig. S17 O1s XPS spectra of different samples.

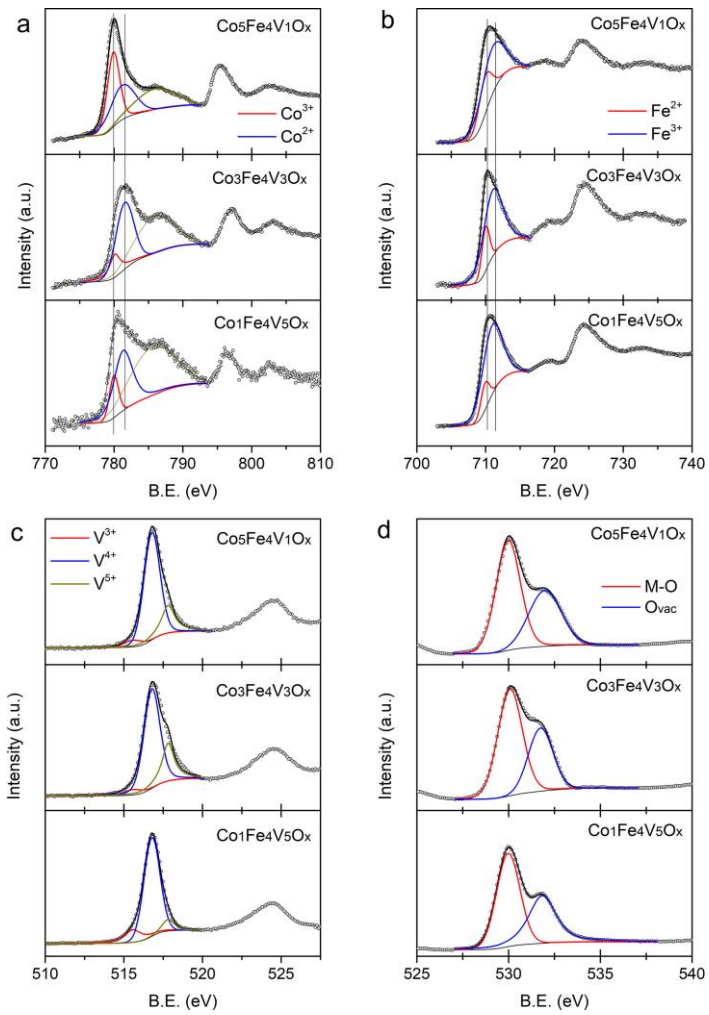

Fig. S18 XPS spectra of (a) Co, (b) Fe, (c) V and (d) O in $Co_1Fe_4V_5O_x$ (top panels) and $Co_5Fe_4V_1O_x$ (bottom panels) samples.

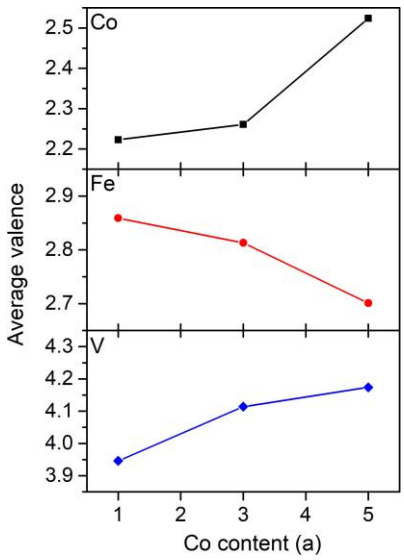

Fig. S19 The relationship between average valence states of different metals and the abundance of Co in various samples with Fe content fixed at 40 at%.

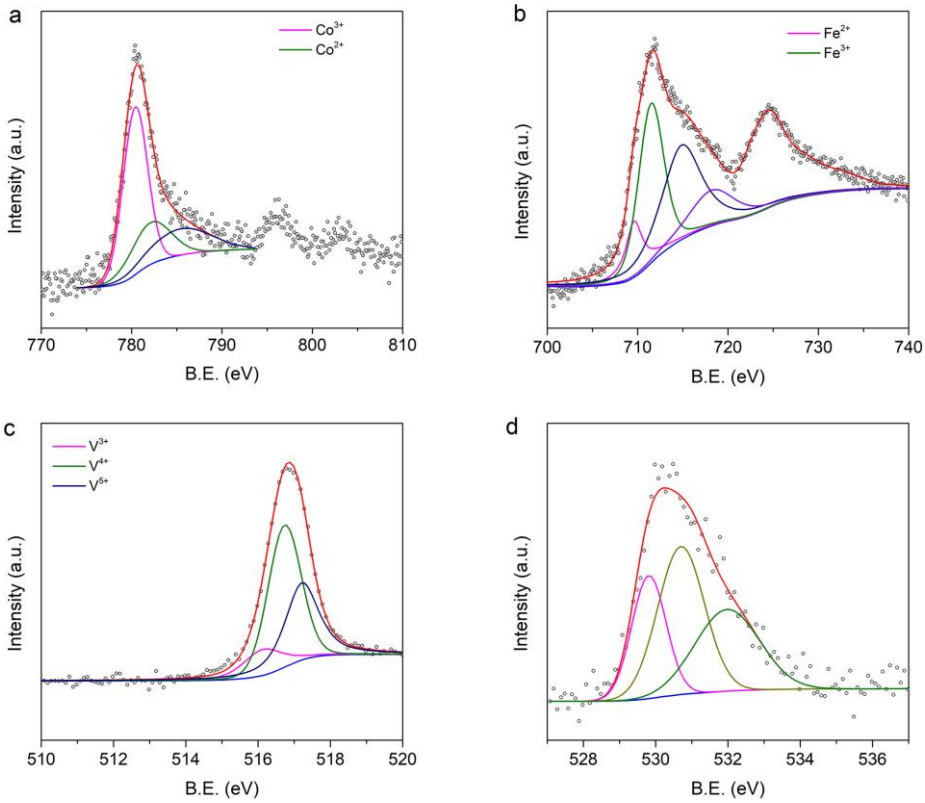

Fig. S20 High-resolution XPS spectra of (a) Co, (b) Fe, and (c) V in $Co_3Fe_4V_3O_x$ after the OER stability test.

Table S8. The valence state of metal species in $Co_3Fe_4V_3O_x$ after the OER stability test determined from XPS analysis (in at%).

Conditions	Co^{2+}	Co^{3+}	Fe^{2+}	Fe^{3+}	V^{3+}	V^{4+}	V^{5+}
Before OER test	73.9	26.1	18.7	81.3	13.2	62.3	24.5
After OER test	29.0	71.0	14.6	85.4	2.3	20.1	77.5