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Supporting Information

Oxygen-Evolution Reactions (OER) on transition-metal-doped $Fe_3Co(PO_4)_4$ iron-phosphate surfaces: A first-principles study

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S1 Ideal energy profile for OER

S2 Pure $Fe_4(PO_4)_4$ surface

S3 Cobalt-Doped Fe_4PO_4

S4 Cobalt-replaced, M-codoped $Fe_3Co_{1-x}M_x(PO_4)_4$ (M = Mn, Os and Ru)

S5 Iron-replaced, M-codoped $Fe_{1-x}M_xCo(PO_4)_4$ (M = Ir, Os and Rh)

S6 Fully relaxed final doped structures

S7. Fully-relaxed doped $Fe_3Co(Po_4)_4$(010) surfaces

S8. Overall trends at the dopant site

Table S1: Energy differences of the overall OER reaction

Table S2: The overpotentials (η) of the different reactive sites

Estimation of free energies of OER reaction sub-steps:

The energies were corrected with zero-point energy (ZPE), with entropy considered from refs. S1 & S2. The overall OER reaction energies are calculated using the following formulae:

For OH*

$$OH\ (sur) - H_2O + \tfrac{1}{2} H_2 - surface = \Delta G_1$$

For O*

$$O\ (sur) + \tfrac{1}{2} H_2 - O_2 + \Delta G_1 = \Delta G_2$$

For OOH*

$$OOH\ (sur) - H_2O + 1/2\ H_2 - O\ (sur) + \Delta G_2 = \Delta G_3$$

For O_2

$$O_2(sur) + \tfrac{1}{2} H_2 - OOH\ (sur) + \Delta G_3 = \Delta G_4$$

Hypothetical, Idealised energy profile

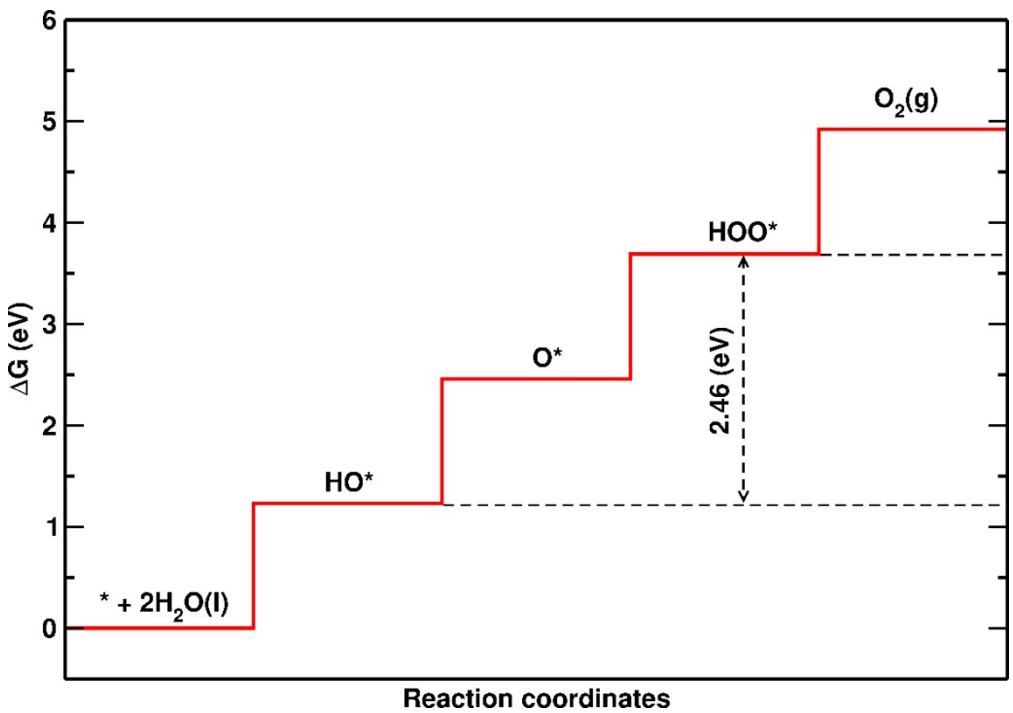

Fig. S1: Ideal energy profile for OER

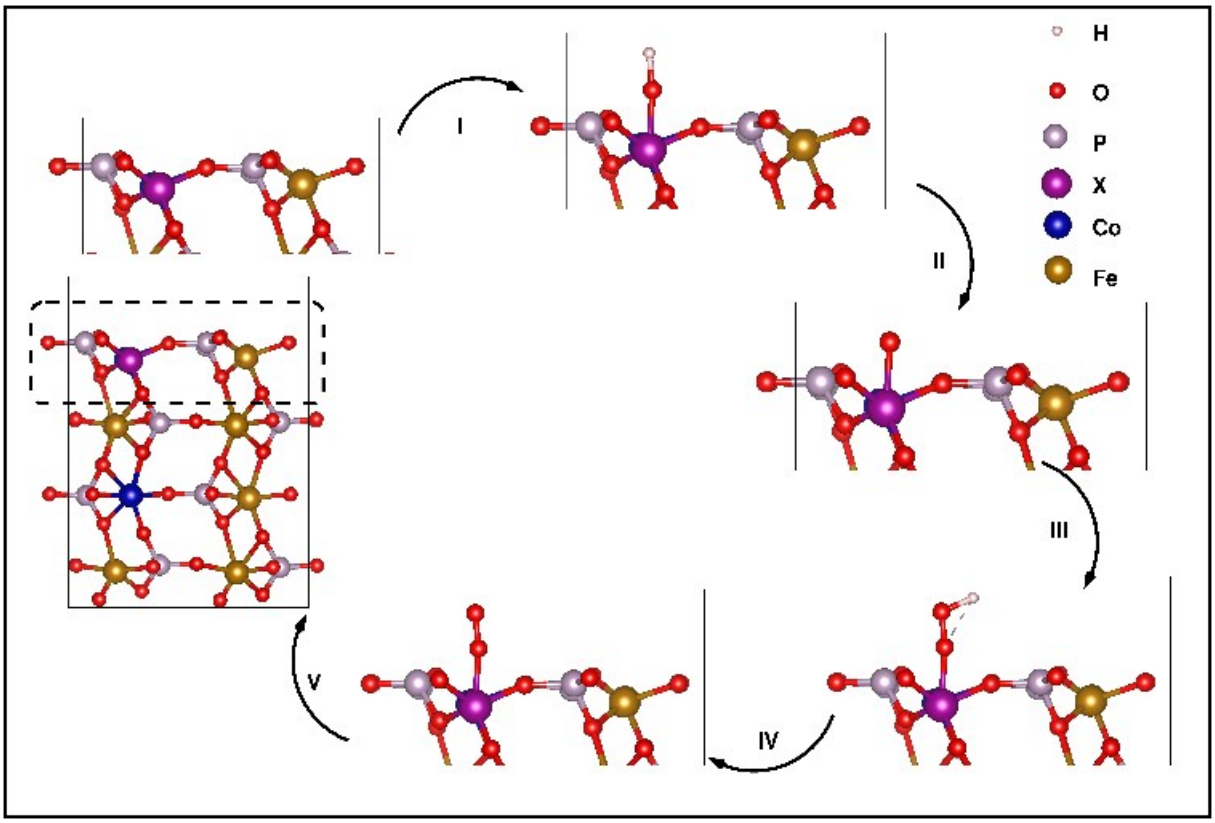

Figure S2. Schematic diagram of the steps involved in OER reaction (for dopants Mn, Os, Ru, Rh and Ir)

<u>Undoped surface of $Fe_4(PO_4)_4$</u>

A and C axis

B and C axis

Red: Oxygen (O)
Golden: Iron (Fe)
Grey: Phosphorus (P)

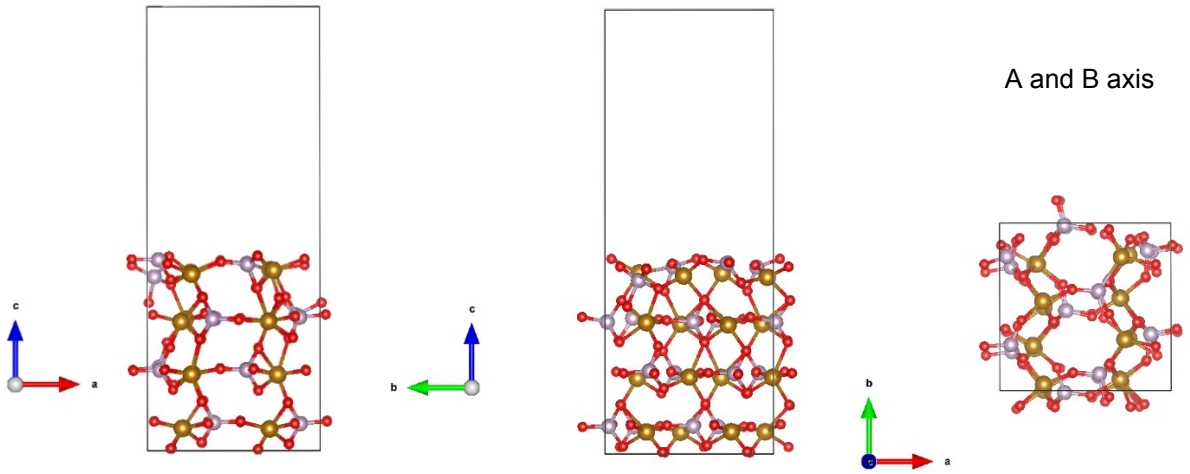

Fig. S3. Views of the undoped (010) surface along different axis viewpoints, including a "bird's-eye" view from atop - on the right-hand side (i.e., along the c-axis, if the a-b axes are in the plane of the page).

<u>Cobalt-Doped $Fe_4(PO_4)_4$ ($Fe_3Co(PO_4)_4$)</u>

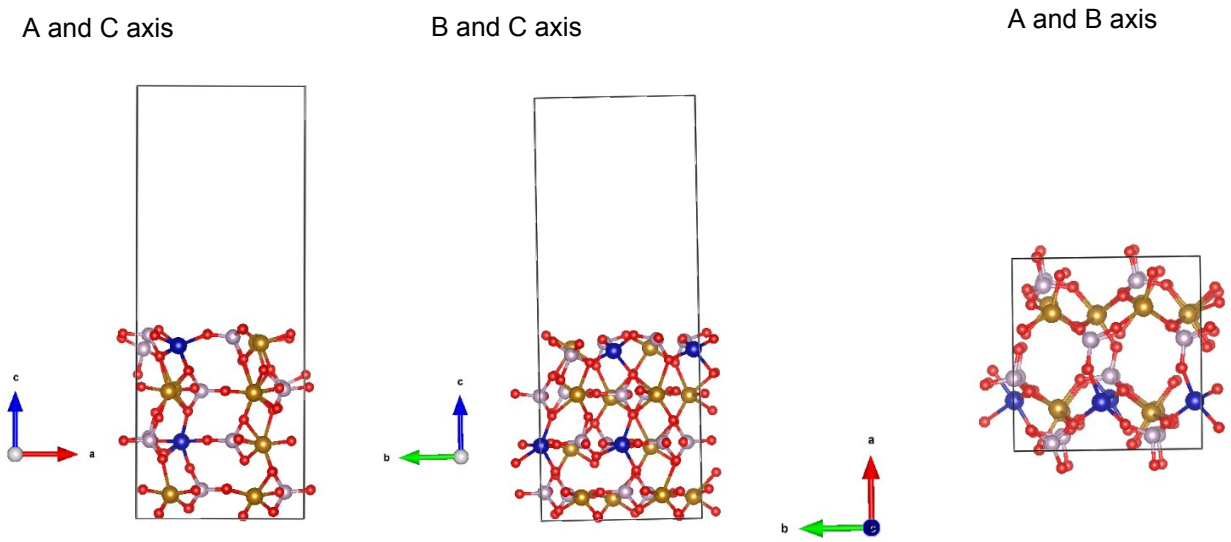

Fig. S4. Views of the cobalt-doped (010) surface along different axis viewpoints, including a "bird's-eye" view from atop - on the right-hand side (i.e., along the c-axis, if the a-b axes are in the plane of the page). The dopant concentration is ~4.16 mol %, and cobalt is in blue, with same colouring otherwise as in Fig. S3.

Cobalt-replaced, M-codoped $Fe_3Co_{1-x}M_x(PO_4)_4$ (M – Mn, Os and Ru)

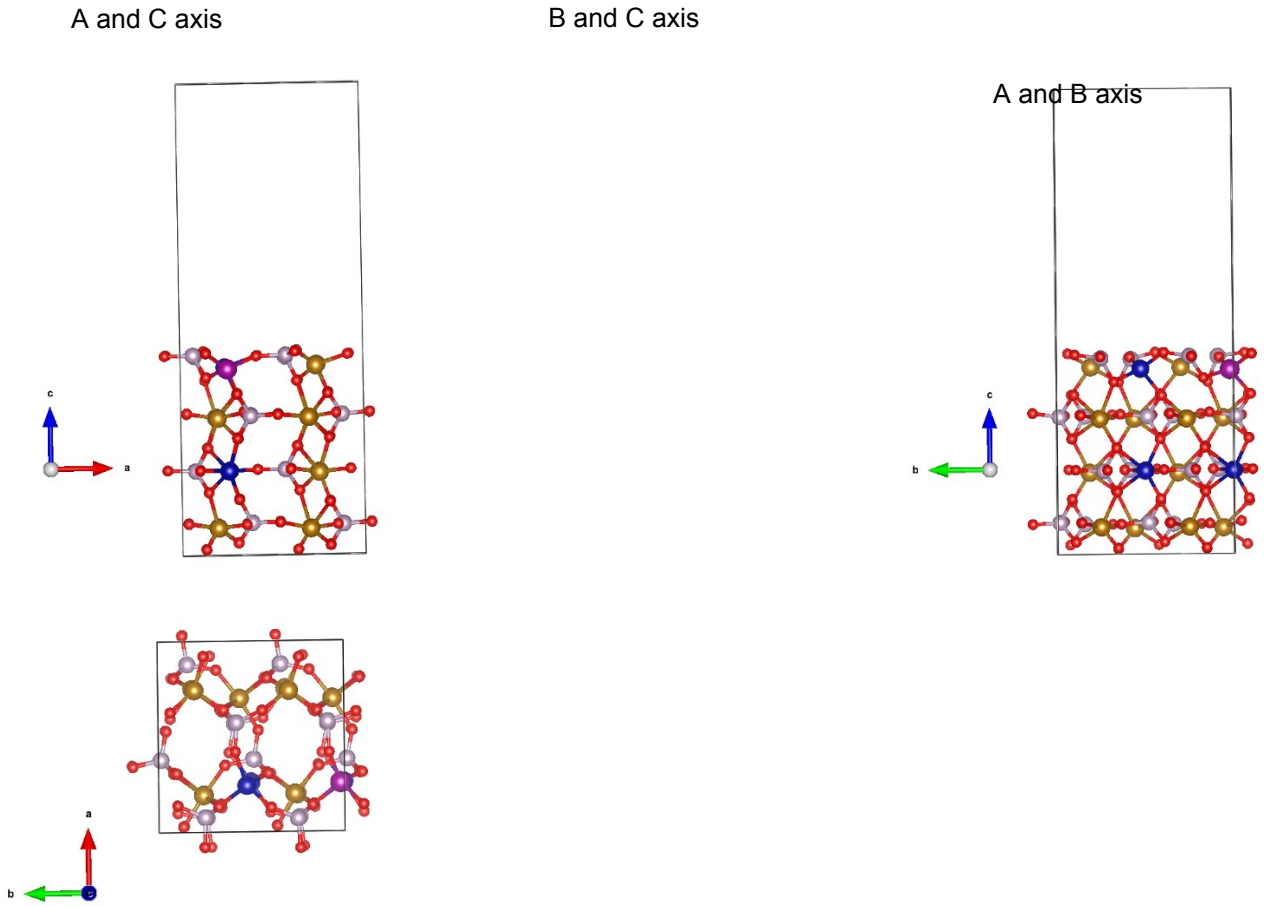

Fig. S5: Perspectives of the cobalt-/'M'-codoped (010) surface along different axis directions, including a "bird's-eye" view from atop - on the right-hand side. The (in-blue) cobalt concentration is 3.125 mol %, whilst (in-purple) transition-metal codopant concentration (replacing cobalt at a surface site) is ~1.04 mol %. The same general atomic colouring applies as in Fig. S3.

Iron-replaced, M-codoped $Fe_{3-x}M_xCo(PO_4)_4$ (M – Ir, Os and Rh)

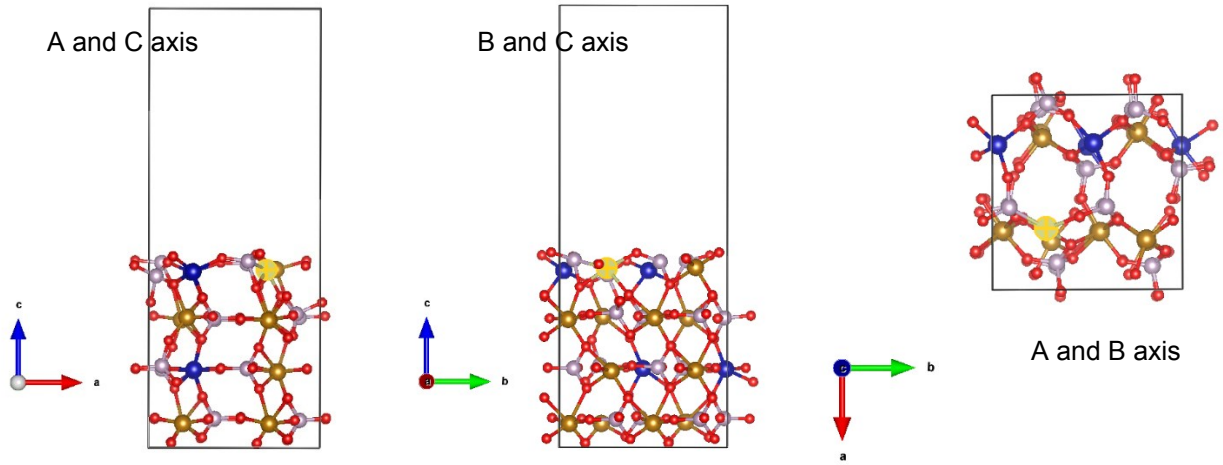

Fig. S6: Perspectives of the iron-replaced, cobalt-/'M'-codoped (010) surface along different axis directions, including "bird's-eye" on the right. The (in-blue) cobalt concentration is 3.125 mol %, whilst the transition-metal codopant, shown by the yellow cross replacing the iron atom at the surface, has a concentration of ~1.04 mol %. The same general atomic colouring applies as in Fig. S3.

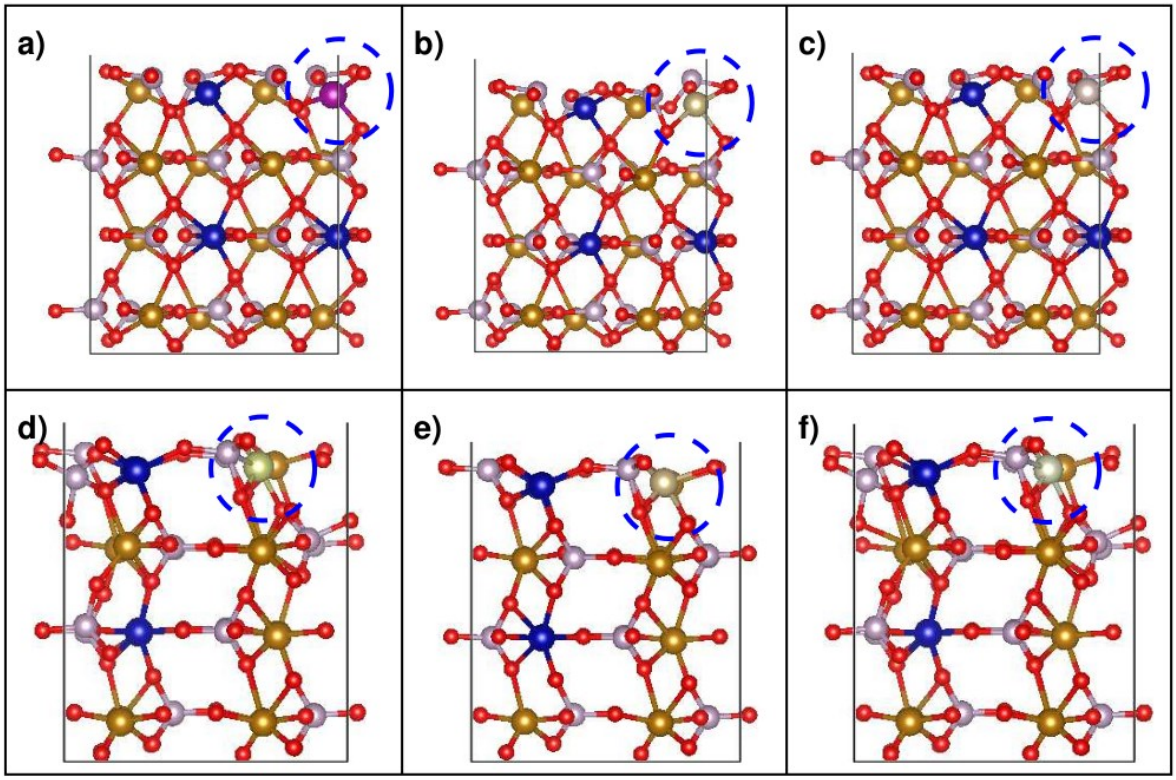

Fig S7. Fully-relaxed doped $Fe_3Co(Po_4)_4(010)$ surfaces, with the dopants shown by dashed blue circles. (a) Cobalt (Co) replaced by Manganese (Mn), (b) Cobalt replaced by Osmium (Os), (c) Cobalt replaced by Ruthenium (Ru), (d) Iron (Fe) replaced by Iridium (Ir), (e) Iron replaced by Osmium (Os), and (f) Iron replaced by Rhodium (Rh).

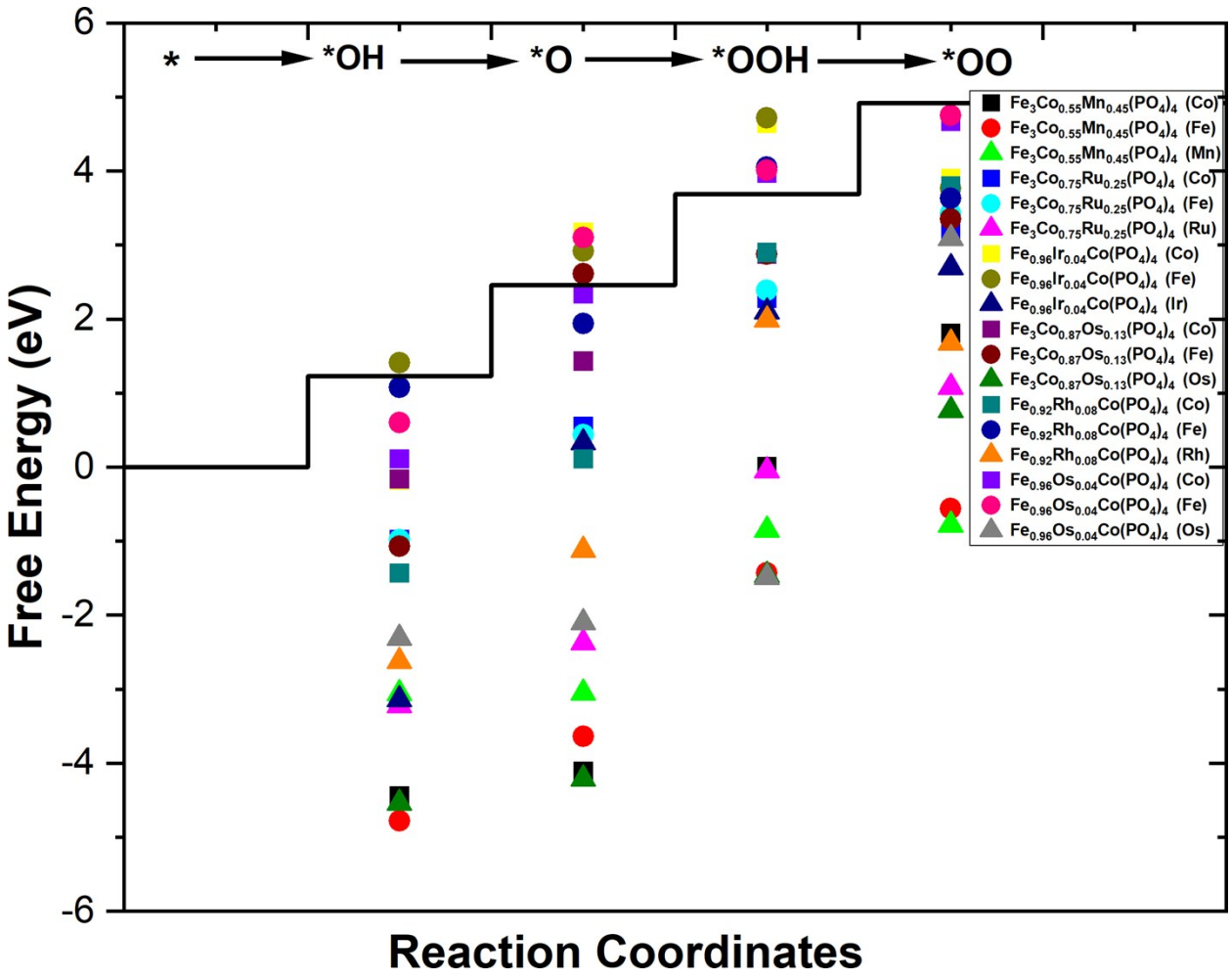

Fig S8. Overall trends at the dopant site, Fe-site, and Co-site for respective OER steps, In Co site (Mn, Co) the Mn is dopant Co is dopant site and this naming pattern is followed for all other sites.

Table S1: Energy differences of the overall OER reaction used the energy profile shown in figures 5-10

Materials	Site	*OH	*O	*OOH	*OO
$Fe_3Co_{0.55}Mn_{0.45}(PO_4)_4$	Co	-4.44	-4.11	0.01	1.81
	Fe	-4.78	-3.64	-1.43	-0.56
	Mn	-3.06	-3.05	-0.85	-0.78
$Fe_3Co_{0.87}Os_{0.13}(PO_4)_4$	Co	0.60	3.10	4.01	4.75
	Fe	0.11	2.34	3.97	4.67
	Os	-2.31	-2.10	-1.49	3.09
	Co	-0.98	0.55	2.28	3.16

$Fe_3Co_{0.75}Ru_{0.25}(PO_4)_4$	Fe	-0.98	0.44	2.39	3.43
	Ru	-3.22	-2.37	-0.05	1.08
$Fe_{0.96}Ir_{0.04}Co(PO_4)_4$	Co	-0.17	3.17	4.64	3.90
	Fe	1.41	2.92	4.72	3.77
	Ir	-3.14	0.33	2.10	2.70
$Fe_{0.92}Rh_{0.08}Co(PO_4)_4$	Co	-1.43	0.11	2.90	3.80
	Fe	1.08	1.94	4.05	3.63
	Rh	-2.62	-1.12	1.99	1.68
$Fe_{0.96}Os_{0.04}Co(PO_4)_4$	Co	-0.16	1.43	2.88	3.76
	Fe	-1.07	2.61	2.88	3.35
	Os	-4.53	-4.21	-1.46	0.77

Table S2: The overpotentials (η) of the different reactive sites

Materials	Site	*OH	*O	*OOH	*OO	O_2	η
$Fe_3Co_{0.55}Mn_{0.45}(PO_4)_4$	Co	-5.67	-0.90	2.89	0.57	1.88	2.89
	Fe	-6.01	-0.09	0.98	-0.36	4.25	4.25
	Mn	-4.29	-1.22	0.97	-1.16	4.47	4.47
$Fe_3Co_{0.87}Os_{0.13}(PO_4)_4$	Co	-0.63	1.27	-0.32	-0.49	-1.06	1.27
	Fe	-1.12	1.00	0.40	-0.53	-0.98	1.00
	Os	-3.54	-1.02	-0.62	3.35	0.60	3.35

$Fe_3Co_{0.75}Ru_{0.25}(PO_4)_4$	Co	-2.21	0.30	0.50	-0.35	0.53	0.53
	Fe	-2.21	0.19	0.72	-0.19	0.26	0.72
	Ru	-4.45	-0.38	1.09	-0.10	2.61	2.61
$Fe_{0.96}Ir_{0.04}Co(PO_4)_4$	Co	-1.40	2.11	0.24	-1.97	-0.21	2.11
	Fe	0.18	0.28	0.57	-2.18	-0.08	0.57
	Ir	-4.37	2.24	0.54	-0.63	0.99	2.24
$Fe_{0.92}Rh_{0.08}Co(PO_4)_4$	Co	-2.66	0.31	1.56	-0.33	-0.11	1.56
	Fe	-0.15	-0.37	0.88	-1.65	0.06	0.88
	Rh	-3.85	0.27	1.88	-1.54	2.01	2.01
$Fe_{0.96}Os_{0.04}Co(PO_4)_4$	Co	-1.39	0.36	0.22	-0.35	-0.07	0.36
	Fe	-2.30	2.45	-0.96	-0.76	0.34	2.45
	Os	-5.76	-0.91	1.52	1.00	2.92	2.92

Coordinates for bulk $Fe_3Co(PO_4)_4$

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Coordinates for $Fe_3Co_{0.75}Ru_{0.25}(PO_4)_4$ surface

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0.2266756076498714	0.0482931568089489	0.4035621109083138

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