Exploring kinetic and thermodynamic aspects of four-electron electrochemical reactions: electrocatalysis of oxygen evolution by metal oxides and biological systems

Vincent C.-C. Wang[1,2]

1. Shouxing Street, Yancheng, Kaohsiung 803, Taiwan (R.O.C)

2. Institute of Chemistry, Academia Sinica, Nangang, Taipei 115, Taiwan (R.O.C)

Supporting information

Figure S1

According to the Rossemeisl *et. al.* paper, the scaling relation between the adsorption energy of HO and HOO over a wide range of metal oxide surface is $\Delta E_{HOO*} = \Delta E_{HO*} + 3.2$ eV.[1] In order to find the relation between the free energy of each reaction step and ΔE_{O*}, the scaling relation between ΔE_{HO*} and ΔE_{O*} is obtained by a linear fitting of ΔE_{HO*} and ΔE_{O*} values over all metal oxides from the same paper. The best fit is $\Delta E_{HO*} = 0.5\Delta E_{O*} - 0.4$ eV as shown in Figure S1. With these two scaling relations and the correction of entropy and zero-point energy contribution, the free energy of each reaction step can be expressed with ΔE_{O*} as follows: $\Delta G_1 = 0.5\Delta E_{O*} - 0.05$ eV, $\Delta G_2 = 0.5\Delta E_{O*} + 0.1$ eV, $\Delta G_3 = -0.5\Delta E_{O*} + 3.15$ eV, $\Delta G_4 = -0.5\Delta E_{O*} + 1.72$ eV.

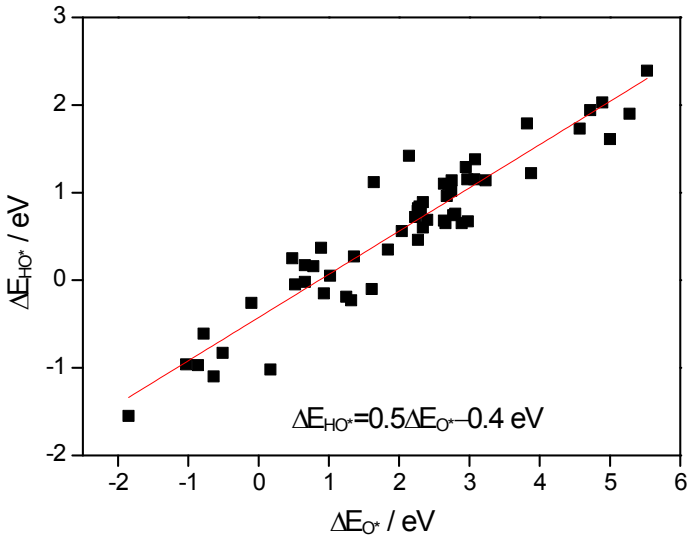

Figure S1 The correlation between calculated ΔE_{HO*} and ΔE_{O*} over a wide range of metal oxide surface. The red line indicates the best fitting line with a square root of

0.9 and a standard deviation of 0.06 eV and 0.02 eV for the slope and intercept respectively.

Figure S2

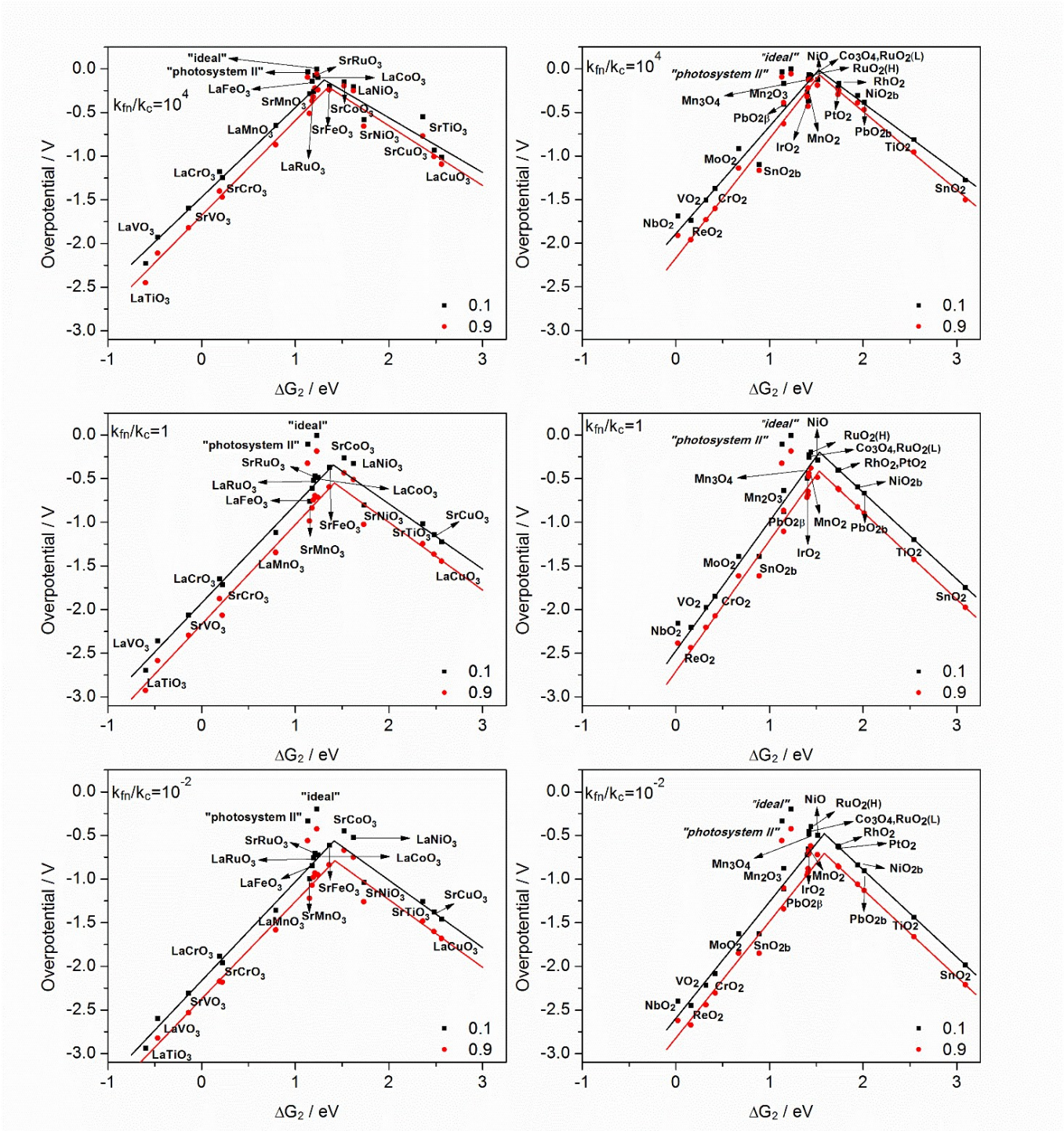

Figure S2 The plot of the overpotential value for the OER against the free energy ΔG_2 when the overpotential value is taken at the current, 0.1 (back square) and 0.9 (red circle). A ratio of k_{fn}/k_c used for simulation is depicted in the figures.

Figure S3

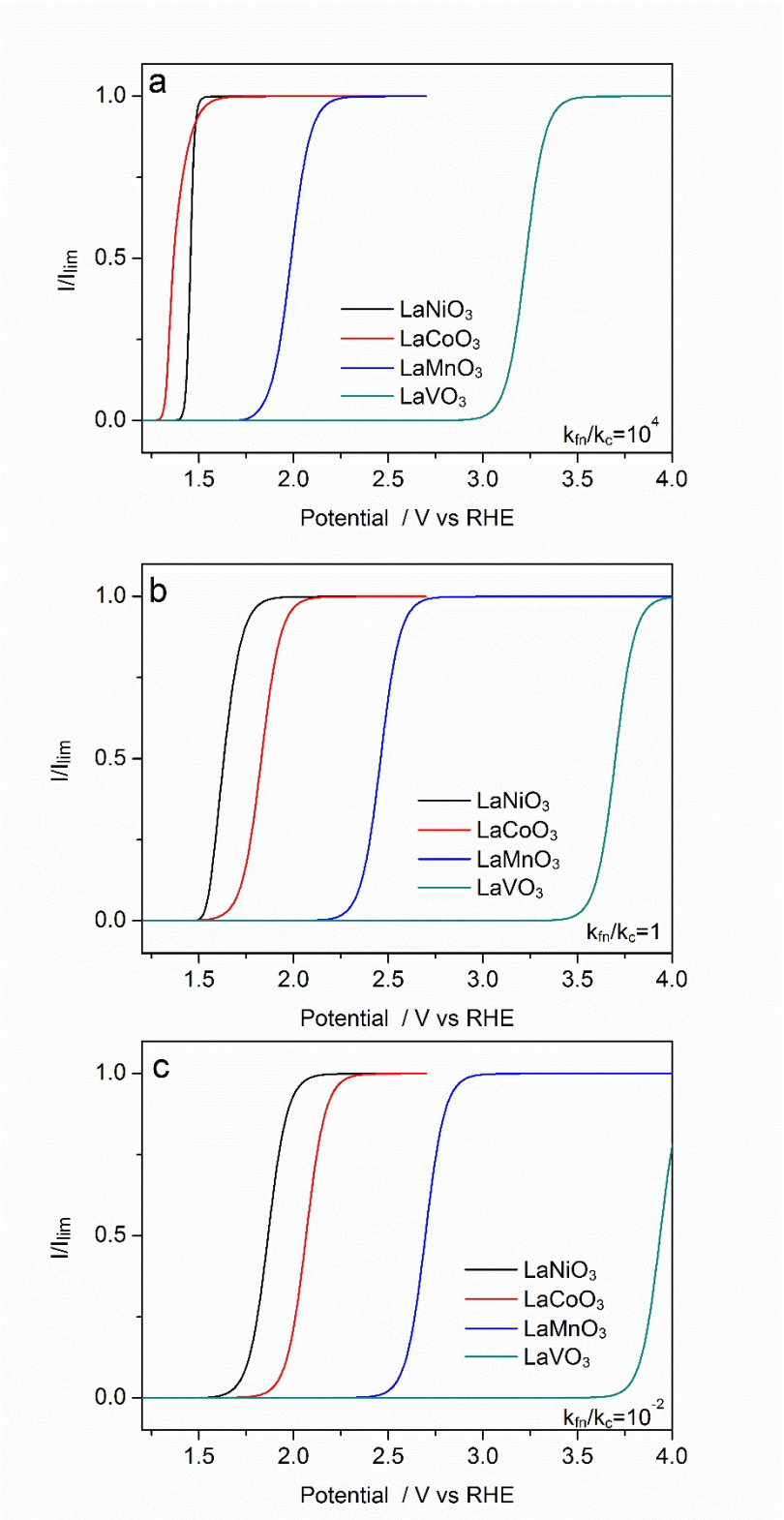
a
1.0
0.5
0.0
I/I_lim
LaNiO3
LaCoO3
LaMnO3
LaVO3
k_fn/k_c=10^4
1.5
2.0
2.5
3.0
3.5
4.0
Potential / V vs RHE
b
1.0
0.5
0.0
I/I_lim
LaNiO3
LaCoO3
LaMnO3
LaVO3
k_fn/k_c=1
1.5
2.0
2.5
3.0
3.5
4.0
Potential / V vs RHE
c
1.0
0.5
0.0
I/I_lim
LaNiO3
LaCoO3
LaMnO3
LaVO3
k_fn/k_c=10^-2
1.5
2.0
2.5
3.0
3.5
4.0
Potential / V vs RHE

Figure S3 The simulation of voltammograms for $LaNiO_3$, $LaCoO_3$, $LaMnO_3$ and $LaVO_3$ with a ratio of $k_{fn}/k_c = 10^4$, 1 and 10^{-2} respectively.

Table S1 The summary of the free energy used for simulations [1] and Tafel slope values obtained from metal oxides and photosystem II studied in this paper.

	Free Energy				Tafel slope (mV/decade) [a]			
	ΔG_1 (eV)	ΔG_2 (eV)	ΔG_3 (eV)	ΔG_4 (eV)	[b] 10^4	[b] 10^2	[b] 1	[b] 10^{-2}
Metal oxide[d]								
$SrTiO_3$	1.57	2.36	0.98	0.01	118(0.5)[c]	133(0.44)	132(0.45)	120(0.49)
$SrVO_3$	0.09	-0.14	3.41	1.56	131(0.45)	132(0.45)	132(0.45)	132(0.45)
$SrCrO_3$	0.72	0.22	3.06	0.92	131(0.45)	132(0.45)	132(0.45)	132(0.45)
$SrMnO_3$	1.17	1.15	2.1	0.5	130(0.45)	132(0.45)	129(0.46)	128(0.46)
$SrFeO_3$	1.64	1.36	1.7	0.22	27(2.19)	30(1.97)	143(0.41); 34(1.74)	130(0.45)
$SrCoO_3$	1.5	1.52	1.44	0.46	27(2.19)	28(2.11)	117(0.50); 33(1.79)	130(0.45)
$SrNiO_3$	2.14	1.73	1.07	-0.02	44(1.34)	50(1.18)	118(0.5)	133(0.44)
$SrCuO_3$	2.29	2.48	0.55	-0.4	43(1.37)	49(1.20)	150(0.39); 68(0.87)	133(0.44)
$SrRuO_3$	1.07	1.21	1.81	0.83	44(1.34)	133(0.44)	133(0.44)	132(0.45)
$LaTiO_3$	-1.2	-0.6	4.04	2.68	114(0.52)	131(0.45)	132(0.45)	123(0.48)
$LaVO_3$	-0.26	-0.47	3.7	1.95	132(0.45)	130(0.45)	131(0.45)	131(0.45)
$LaCrO_3$	0.52	0.19	2.99	1.22	131(0.45)	132(0.45)	132(0.45)	132(0.45)
$LaMnO_3$	0.62	0.79	2.46	1.05	120(0.49)	131(0.45)	132(0.45)	132(0.45)
$LaFeO_3$	1.14	1.1775	1.9525	0.65	174(0.34); 64(0.92)	131(0.45)	131(0.45)	131(0.45)
$LaCoO_3$	1.45	1.24	1.83	0.4	111(0.53)	133(0.44)	131(0.45)	132(0.45)
$LaNiO_3$	1.5	1.62	1.5	0.3	27(2.19)	33(1.79)	118(0.5); 39(1.51)	130(0.45)
$LaCuO_3$	2.38	2.56	0.46	-0.48	44(1.34)	48(1.23)	151(0.39); 59(1)	131(0.45)
$LaRuO_3$	0.7	1.19	1.86	1.17	34(1.74)	146(0.4); 49(1.20)	131(0.45)	131(0.45)
--	--	--	--	--	--	--	--	--
Photosystem II[d]	1.2	1.13	1.44	1.15	29(2.03)	35(1.69)	59(1); 158(0.37)	131(0.45)
optimal	1.23	1.23	1.23	1.23	35(1.69)	28(2.11)	30(1.97); 136(0.43)	131(0.45)

	Free energy				Tafel slope (mV/decade) [a]			
	ΔG_1 (eV)	ΔG_2 (eV)	ΔG_3 (eV)	ΔG_4 (eV)	[b] 10^4	[b] 10^2	[b] 1	[b] 10^{-2}
Metal oxide[d]								
MoO_2	0.4	0.67	2.73	1.12	130(0.45)[c]	132(0.45)	130(0.45)	131(0.45)
lrO_2	0.25	1.41	1.76	1.5	33(1.79)	35(1.69)	49(1.20); 131(0.45)	132(0.45)
RuO_2 (high coverage)	1.31	1.42	1.59	0.6	31(1.90)	42(1.40)	69(0.86); 161(0.37)	132(0.45)
PtO_2	1.09	1.73	--	--	44(1.34)	46(1.28)	56(1.05); 152(0.39)	132(0.45)
RhO_2	1.11	1.74	1.31	0.76	44(1.34)	51(1.16)	69(0.86); 140(0.42)	132(0.45)
NbO_2	-0.48	0.02	3.5	1.88	132(0.45)	132(0.45)	132(0.45)	132(0.45)
ReO_2	-0.75	0.16	3.55	1.96	118(0.5)	131(0.45)	132(0.45)	132(0.45)
VO_2	0.51	0.32	3.32	0.77	132(0.45)	131(0.45)	132(0.45)	132(0.45)
MnO_2	1.73	1.4	1.8263	-0.0363	27(2.19)	39(1.51)	131(0.45)	132(0.45)
CrO_2	1.77	0.42	3.18601	-0.45601	132(0.45)	132(0.45)	132(0.45)	132(0.45)
NiO_{2b}	1	1.94	1.3157	0.6643	45(1.31)	50(1.18); 133(0.44)	131(0.45)	133(0.44)
PbO_{2b}	1.02	2.01	1.4109	0.4791	44(1.34)	51(1.16); 135(0.44)	131(0.45)	131(0.45)
SnO_{2b}	-0.67	0.89	2.7309	1.9691	34(1.74)	54(1.09); 142(0.42)	130(0.45)	131(0.45)
Mn_3O_4	1.04	1.41	1.8	0.67	46(1.28)	66(0.89); 152(0.39)	132(0.45)	132(0.45)
Mn_2O_3(II)	1.19	1.15	1.98	0.6	77(0.77); 147(0.40)	132(0.45)	131(0.45)	131(0.45)
Co_3O_4	1.37	1.42	1.55	0.58	27(2.19)	33(1.79)	131(0.45)	131(0.45)
TiO_2	2.74	2.84	--	--	44(1.34)	45(1.31)	48(1.23); 121(0.49)	131(0.45)
SnO_2	2.25	3.08	--	--	131(0.45)	131(0.45)	132(0.45)	132(0.45)
$PtO_{2\beta}$	1.17	1.19	1.8342	0.7258	48(1.23); 148(0.40)	130(0.45)	131(0.45)	132(0.45)
RuO_2 (low coverage)	0.95	1.44	1.48	1.05	23(2.57)	41(1.44)	50(1.18); 136(0.43)	130(0.45)
--	--	--	--	--	--	--	--	--
Photosystem II[d]	1.2	1.13	1.44	1.15	29(2.03)	35(1.69)	59(1); 158(0.37)	131(0.45)
optimal	1.23	1.23	1.23	1.23	35(1.69)	28(2.11)	30(1.97); 136(0.43)	131(0.45)

a. The Tafel slope is obtained from the logarithm of current between −2.3 and −0.3.

b. The ratio of k_{fn}/k_c for simulated voltammograms.

c. The value inside the parentheses is the apparent transfer coefficient.

d. The adsorption energy for each metal oxide are obtained from the Table 2 of supporting materials of the reference 1 and the values for photosystem II are obtained from the Table 1 of the reference 2.

Figure S4

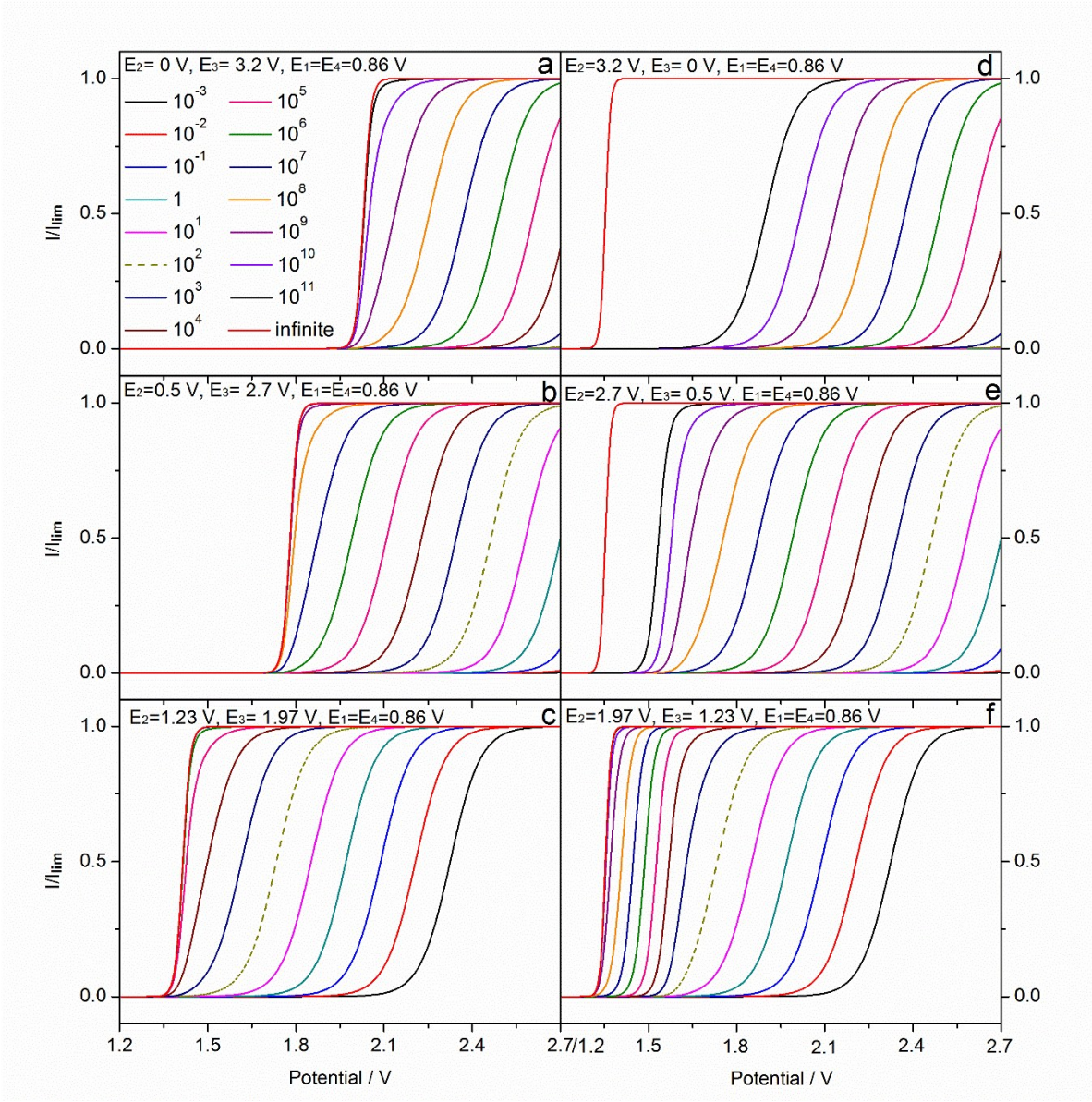

Figure S4 Simulation of voltammograms with a universal scaling relation $\Delta G_2 + \Delta G_3$ =3.2 eV. The equilibrium potentials E_1=E_4=0.86 V were used to simulate voltammograms with varying E_2 and E_3 values. The ratio of k_{fn}/k_c for simulations is indicated in Figure S4a.

Figure S5

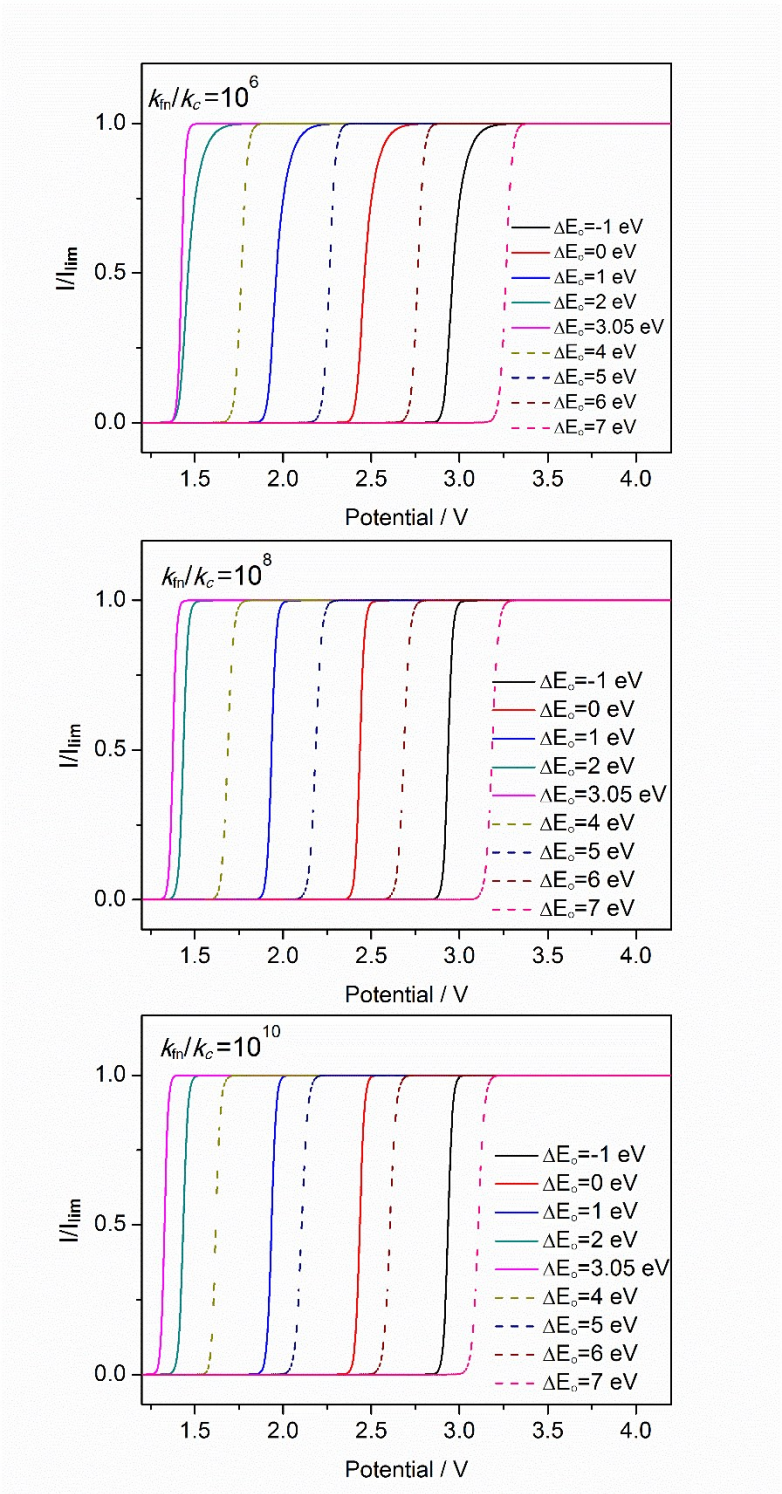

Figure S5 The effect of the adsorption energy of the intermediate species, oxygen on the activity of OER electrocatalysts.

Table S2 The summary of the Tafel slope from Figure 5 and Figure S5.

	ΔE_{O*} (eV)									
k_{fn}/k_2	**-2**	**-1**	**0**	**1**	**2**	**3.05**	**4**	**5**	**6**	**7**
10^{-2}	132 (0.45)[a]	132 (0.45)	132 (0.45)	132 (0.45)	132 (0.45)	129 (0.46)	131 (0.45)	131 (0.45)	131 (0.45)	131 (0.45)
1	132 (0.45)	132 (0.45)	132 (0.45)	132 (0.45)	132 (0.45)	54 (1.09); 176 [b] (0.34)	72 (0.82); 171 (0.35)	65 (0.91); 156 (0.38)	88 (0.67); 229 (0.26)	72 (0.82); 129 (0.46)
10^{2}	132 (0.45)	132 (0.45)	132 (0.45)	132 (0.45)	131 (0.45)	38 (1.55)	45 (1.31)	47 (1.26)	46 (1.28)	46 (1.28)
10^{4}	119 (0.50)	114 (0.52)	119 (0.50)	120 (0.49)	118 (0.5)	29 (2.03)	44 (1.34)	43 (1.37)	43 (1.37)	44 (1.34)
10^{6}	45 (1.31)	44 (1.34)	44 (1.34)	45 (1.31)	44 (1.34)	27 (2.19)	45 (1.31)	44 (1.34)	44 (1.34)	44 (1.34)
10^{8}	33 (1.79)	33 (1.79)	33 (1.79)	33 (1.79)	33 (1.79)	26 (2.27)	37 (1.59)	44 (1.34)	44 (1.34)	44 (1.34)
10^{10}	33 (1.79)	33 (1.79)	33 (1.79)	33 (1.79)	33 (1.79)	26 (2.27)	28 (2.11)	44 (1.34)	44 (1.34)	44 (1.34)
infinite	33 (1.79)	34 (1.74)	33 (1.79)	33 (1.79)	34 (1.74)	21 (2.81)	21 (2.81)	21 (2.81)	21 (2.81)	21 (2.81)

[a] The unit for the Tafel slope inside Table S2 is mV/decade. The Tafel slope is obtained from the logarithm of current between − 2.3 and –0.3. The value inside the parentheses is the apparent transfer coefficient.

[b] Two Tafel slopes were obtained and the smaller value showed first.

The free energy values for NiOOH and Ni_xFe_yOOH

According to the paper reported by Bell, Nørskov and their co-workers,[3] the scaling relation for pure or doped γ-FeOOH and γ-NiOOH can be described as follows: $\Delta E_{O*}=1.2\Delta E_{HO*}+1.9$ eV and $\Delta E_{HOO*}=0.83\Delta E_{HO*}+3.29$ eV. After correcting contribution from entropy and zero potential energy, the free energy for each step can be described as follows: $\Delta G_1=\Delta E_{HO*}+0.44$ eV, $\Delta G_2=0.2\Delta E_{HO*}+1.56$ eV, $\Delta G_3=-0.37\Delta E_{HO*}+1.83$ eV, $\Delta G_4=-0.83\Delta E_{HO*}+1.09$ eV.

References

1.I. C. Man, H. Y. Su, F. Calle-Vallejo, H. A. Hansen, J. I. Martinez, N. G. Inoglu, J. Kitchin, T. F. Jaramillo, J. K. Norskov and J. Rossmeisl, *Chemcatchem*, 2011, 3, 1159-1165.

2.J. Rossmeisl, K. Dimitrievski, P. Siegbahn and J. K. Norskov, *Journal of Physical Chemistry C*, 2007, 111, 18821-18823.

3.D. Friebel, M. W. Louie, M. Bajdich, K. E. Sanwald, Y. Cai, A. M. Wise, M. J. Cheng, D. Sokaras, T. C. Weng, R. Alonso-Mori, R. C. Davis, J. R. Bargar, J. K. Norskov, A. Nilsson and A. T. Bell, *J. Am. Chem. Soc.*, 2015, 137, 1305-1313.