Hydroxyl Group Modification Improves the Electrocatalytic ORR and OER Activity of Graphene Supported Single and Bi-metal Atomic Catalysts (Ni, Co, Fe)

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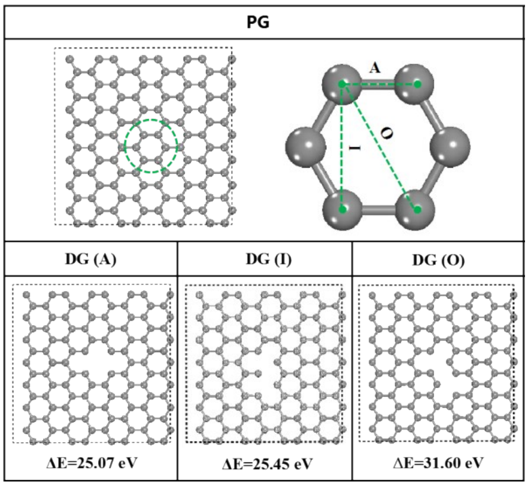
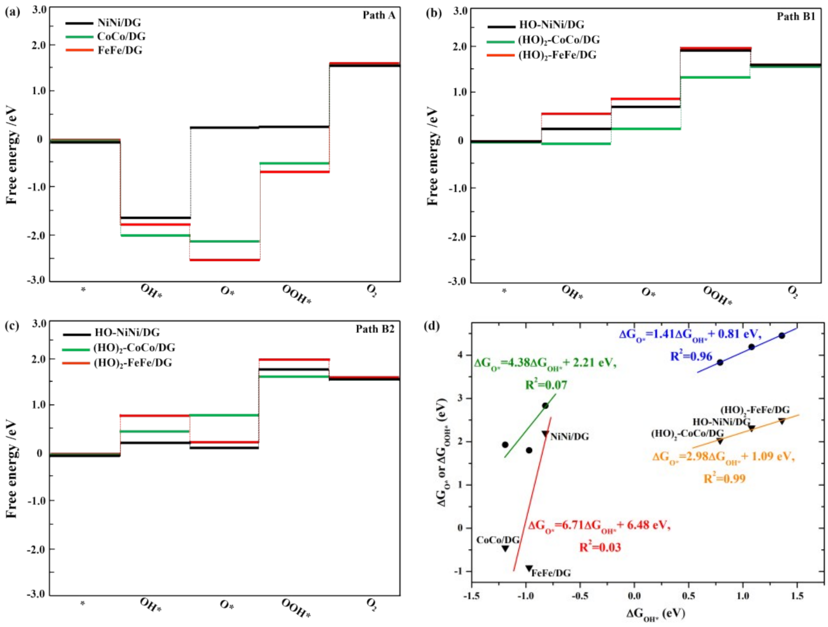


Figure S1. The optimized geometrical structures of defective graphene in top views, mainly including the DG (O, I and P).



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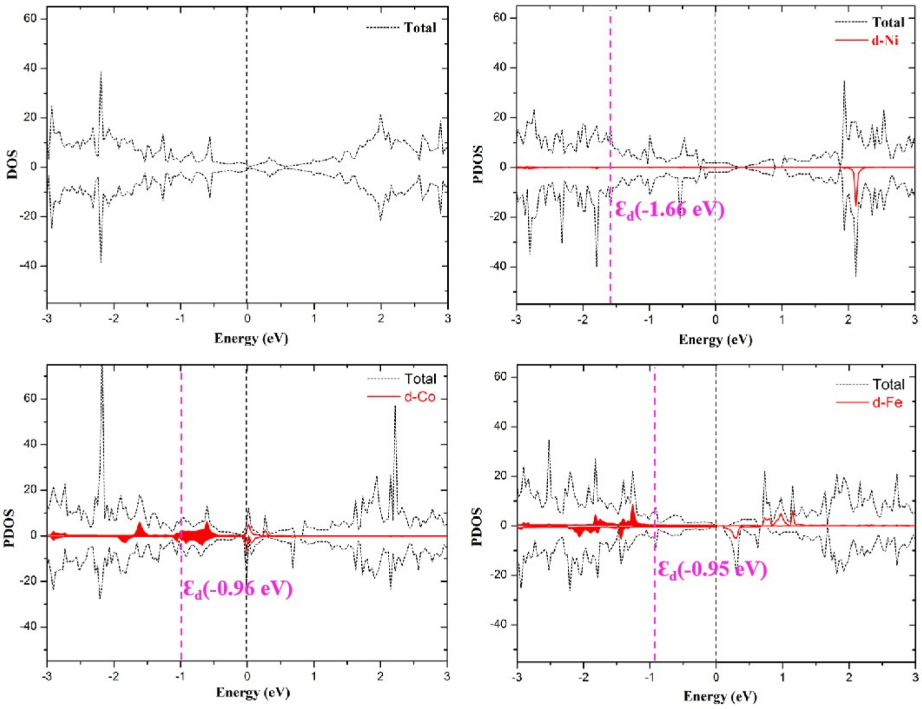
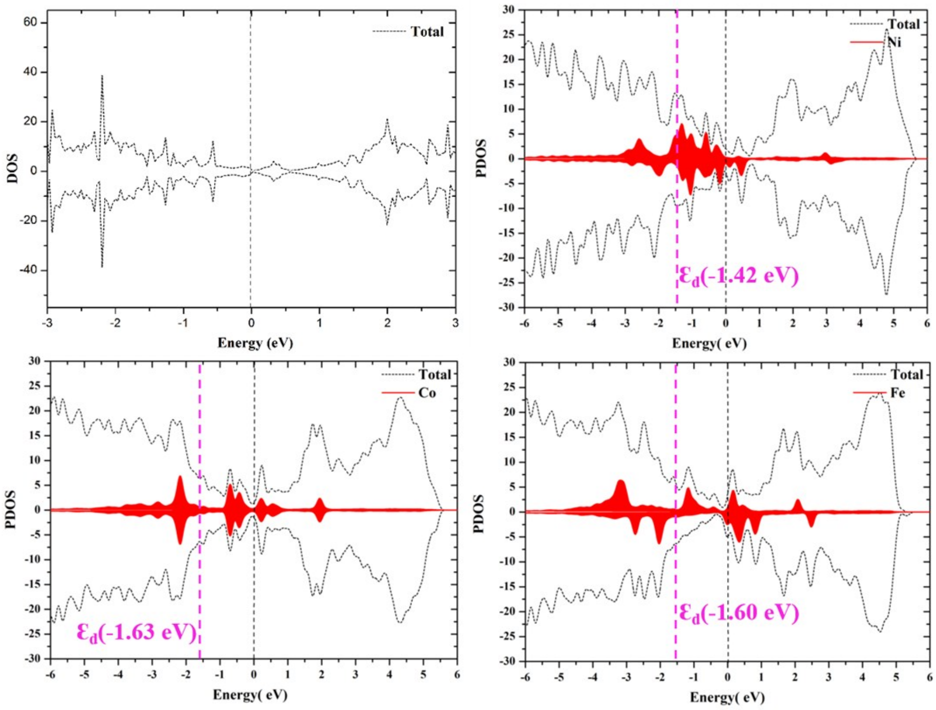


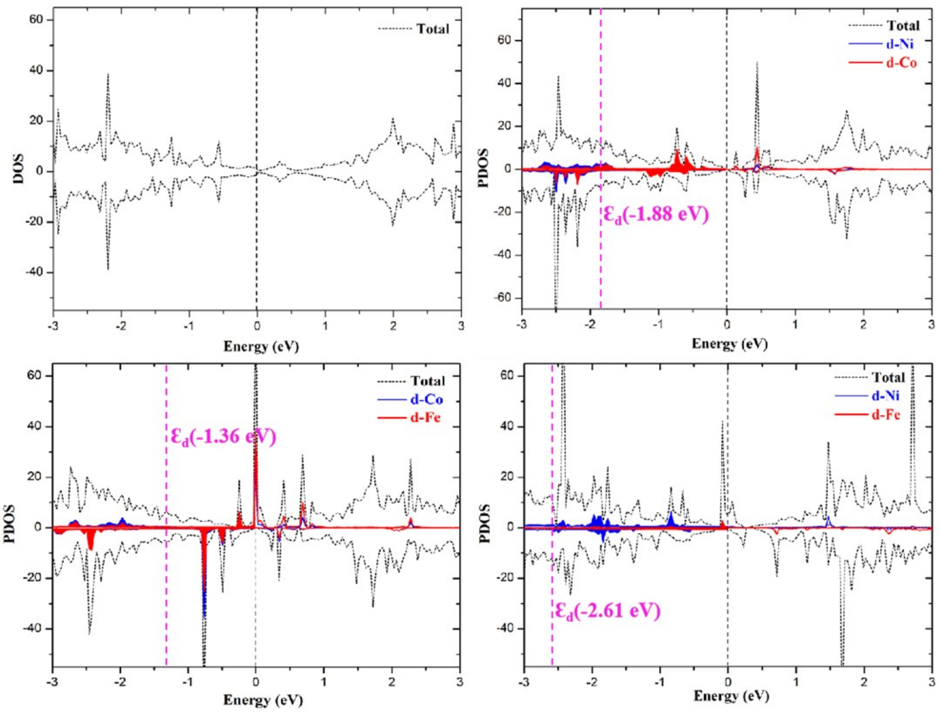
Total
DOS
Energy (eV)
d-Ni
PDOS
εd(-1.66 eV)
d-Co
εd(-0.96 eV)
d-Fe
εd(-0.95 eV)

(a)



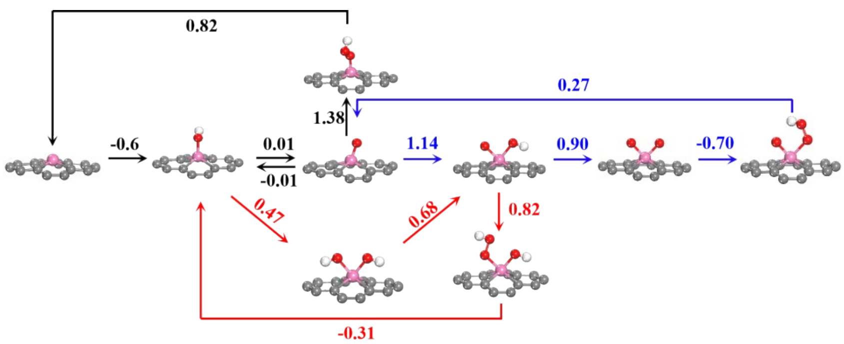
Total
DOS
Energy (eV)
Ni
PDOS
εd(-1.42 eV)
Energy(eV)
Co
εd(-1.63 eV)
Fe
εd(-1.60 eV)

(b)

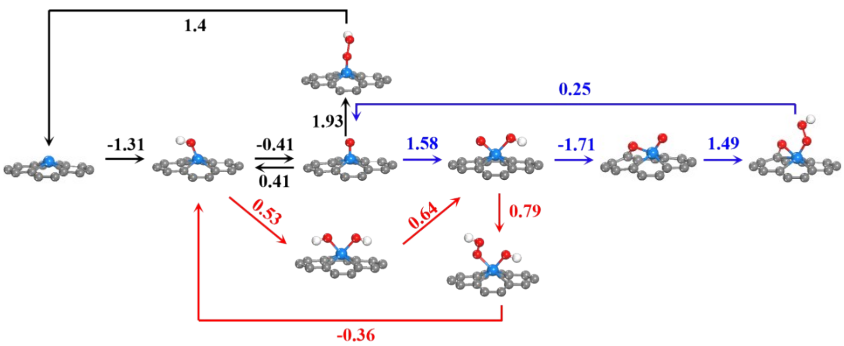


(c)

Figure S3. The project density of states (PDOS) of the d-orbitals of the transition metal atom (M) on bare M/DG and M^1M^2/DG. (a) The PDOS of d-orbitals of the M on bare M/DG. (b) The PDOS of d-orbitals of the M on bare MM/DG. (c) The PDOS of d-orbitals of the M^1 and M^2 on bare M^1M^2/DG. Pink dotted line denoted the d-band center of transition metal atom M.



(a)



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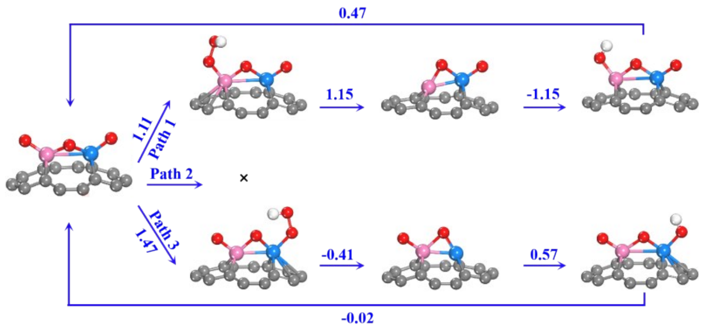

(c)

Figure S4. (a) The ΔG (eV) of the various reactions and all intermediates configurations of OER and ORR process on Co/DG. (b) The ΔG (eV) of the various reactions and all intermediates configurations of OER and ORR process on Fe/DG. (c) The ΔG (eV) of the various reactions and all intermediates configurations of OER and ORR process on $(O)_3$-CoFe/DG.

Table S1. The ΔE_{ads} (eV) and ΔG_{ads} (eV) of oxygenated intermediates involved in OER and ORR on bare and hydroxylated M/DG.

Oxygenated Intermediates	Ni/DG (eV)	Co/DG (eV)	Fe/DG (eV)
	M center of M/DG		
ΔE_{OH*}	0.71	–0.06	–0.77
ΔG_{OH*}	0.99	0.22	–0.48
ΔE_{O*}	2.47	1.05	–0.08
ΔG_{O*}	2.48	1.06	–0.07
ΔE_{OOH*}	3.75	3.04	2.47
ΔG_{OOH*}	3.98	3.27	2.69
ΔE_{O2*}	–0.08	–0.90	–1.20
ΔG_{O2*}	–0.07	–0.89	–1.19
	M center of HO-M/DG		
ΔE_{OH*}	–	0.93	0.99
ΔG_{OH*}	–	1.3	1.35

ΔE_{O*}	–	2.85	2.88
ΔG_{O*}	–	2.87	2.82
ΔE_{OOH*}	–	4.05	4.11
ΔG_{OOH*}	–	4.45	4.44
ΔE_{O2*}	–	0.28	0.65
ΔG_{O2*}	–	0.51	0.88

Table S2. The ΔE_{ads} (eV) and ΔG_{ads} (eV) of oxygenated intermediates involved in OER and ORR on bare and hydroxylated MM/DG.

Oxygenated Intermediates	NiNi/DG	CoCo/DG (eV)	FeFe/DG (eV)
*M-M bridge center of MM/D*G			
ΔE_{OH*}	–1.11	–1.48	–1.26
ΔG_{OH*}	–0.82	–1.19	–0.97
ΔE_{O*}	1.99	–0.46	–0.92
ΔG_{O*}	2.00	–0.45	–0.91
ΔE_{OOH*}	2.61	1.71	1.58
ΔG_{OOH*}	2.83	1.93	1.80
ΔE_{O2*}	–1.95	–1.68	–1.84
ΔG_{O2*}	–1.94	–1.67	–1.83
M center / M-M bridge center of $(HO)_2$-MM/DG			
ΔE_{OH*}	0.72	0.33/0.84	0.91/1.11
ΔG_{OH*}	1.08	0.79/1.30	1.36/1.56
ΔE_{O*}	2.38/1.86	1.95/2.31	2.41/1.87
ΔG_{O*}	2.32/1.89	2.03/2.40	2.49/1.95
ΔE_{OOH*}	3.85/3.89	3.45/3.76	4.07/4.01
ΔG_{OOH*}	4.19/4.23	3.83/4.15	4.45/4.39
ΔE_{O2*}	–0.23/–0.65	–1.12/–0.30	–0.36/–0.01
ΔG_{O2*}	0.00/–0.09	–0.56/0.26	0.20/0.55

Table S3. The ΔE_{ads} (eV) and ΔG_{ads} (eV) of oxygenated intermediates involved in OER and ORR process on bare and hydroxylated M^1M^2/DG.

Oxygenated Intermediates	NiCo/DG (eV)	CoFe/DG (eV)	NiFe/DG (eV)
M^1-M^2 bridge center of M^1M^2/DG			
ΔE_{OH*}	–1.28	–1.78	–0.26
ΔG_{OH*}	–0.99	–1.49	0.03
ΔE_{O*}	–0.35	–0.95	0.78
ΔG_{O*}	–0.35	–0.94	0.79
ΔE_{OOH*}	1.98	1.52	3.00

ΔG_{OOH*}	2.20	1.74	3.23
ΔE_{O2*}	–1.49	–1.97	–1.68
ΔG_{O2*}	–1.48	–1.96	–1.67
M^1 center / M^1-M^2 bridge center / M^2 center of $(HO)_2$-M^1M^2/DG			
ΔE_{OH*}	0.50/0.38/0.10	0.67/0.74/0.22	0.86/0.57/–0.41
ΔG_{OH*}	0.96/0.84/0.54	1.12/1.19/0.68	1.31/1.02/0.04
ΔE_{O*}	2.75/1.73/1.69	2.24/1.49/1.45	3.05/1.50/0.45
ΔG_{O*}	2.83/1.82/1.77	2.32/1.57 /1.53	3.13/1.58/0.53
ΔE_{OOH*}	3.73/3.36/3.42	3.68/3.57 /3.11	3.62/3.13/2.15
ΔG_{OOH*}	4.12/3.74/3.80	4.06/3.96 /3.49	4.00/3.51/2.53
ΔE_{O2*}	–0.80/–0.60/–1.41	–0.83/–0.49/–1.38	–0.53/–0.77/–2.14
ΔG_{O2*}	–0.24/–0.04/–0.85	–0.27/0.07/–0.82	0.03/–0.21/–1.58

Table S4. The ΔG of various reactions (eV) and η (V) for the OER and ORR process over bare and hydroxylated M/DG.

Reactions	ΔG(eV)	η(V)	ΔG(eV)	η(V)	ΔG(eV)	η(V)
	Ni/DG		Co/DG		Fe/DG	
M center of M/DG						
$OH^- + * \rightarrow OH^* + e^-$	0.17	η^{OER}=0.27	–0.6	η^{OER}=0.98	–1.31	η^{OER}=1.53
$OH^- + OH^* \rightarrow O^* + H_2O + e^-$	0.66		0.01		–0.41	
$OH^- + O^* \rightarrow OOH^* + e^-$	0.67	η^{ORR}=0.29	1.38	η^{ORR}=1.00	1.93	η^{ORR}=1.71
$OH^- + OOH^* \rightarrow * + O_2 + H_2O + e^-$	0.11		0.82		1.4	
M center of HO-M/DG						
$OH^- + * \rightarrow OH^* + e^-$	–	–	0.47	η^{OER}=0.36	0.53	η^{OER}=0.39
$OH^- + OH^* \rightarrow O^* + H_2O + e^-$	–		0.68		0.64	
$OH^- + O^* \rightarrow OOH^* + e^-$	–	–	0.77	η^{ORR}=0.71	0.79	η^{ORR}=0.76
$OH^- + OOH^* \rightarrow * + O_2 + H_2O + e^-$	–		–0.31		–0.36	

Table S5. The ΔG of various reactions (eV) and η (V) for the OER and ORR process over bare and hydroxylated MM/DG.

Reactions	ΔG(eV)	η(V)	ΔG(eV)	η(V)	ΔG(eV)	η(V)
	NiNi/DG		CoCo/DG		FeFe/DG	
M-M bridge center of MM/DG						
OH^-+*→OH*+e^-	–1.65	η^{OER}=1.59	–2.02	η^{OER}=1.76	–1.80	η^{OER}=1.88
OH^-+OH*→O*+H_2O+e^-	1.99		–0.09		–0.77	
OH^-+O*→OOH*+e^-	0.01	η^{ORR}=2.05	1.55	η^{ORR}=2.42	1.88	η^{ORR}=2.20
OH^-+OOH*→*+O_2+H_2O+e^-	1.26		2.16		2.29	
M center / M-M bridge center of $(HO)_2$-MM/DG						
OH^-+*→OH*+e^-	0.25	η^{OER}=0.64/1.19	–0.04/0.47	η^{OER}=0.57/0.52	0.53/0.74	η^{OER}=0.73/1.22
OH^-+OH*→O*+H_2O+e^-	0.42/–0.10		0.41/0.27		0.31/–0.44	
OH^-+O*→OOH*+e^-	1.04/1.59	η^{ORR}=0.51/0.54	0.97/0.92	η^{ORR}=0.44/0.45	1.13/1.62	η^{ORR}=0.76/0.84
OH^-+OOH*→*+O_2+H_2O+e^-	–0.10/–0.14		0.26/–0.05		–0.37/–	

Table S6. The ΔG of various reactions (eV) and η (V) for the OER and ORR process over bare and hydroxylated $(HO)_2$-NiCo/DG.

Reactions	ΔG(eV)	η(V)
Ni-Co bridge center of NiCo/DG		
OH^-+*→OH*+e^-	–1.82	η^{OER}=1.49
OH^-+OH*→O*+H_2O+e^-	–0.18	
OH^-+O*→OOH*+e^-	1.72	η^{ORR}=2.22
OH^-+OOH*→*+O_2+H_2O+e^-	1.89	
Ni center / Ni-Co bridge center / Co center of $(HO)_2$-NiCo/DG		
OH^-+*→OH*+e^-	0.13/0.01/–0.27	η^{OER}=0.64/0.69/0.81
OH^-+OH*→O*+H_2O+e^-	1.04/0.15/0.38	
OH^-+O*→OOH*+e^-	0.46/1.09/1.21	η^{ORR}=0.43/0.39/0.67
OH^-+OOH*→*+O_2+H_2O+e^-	–0.03/0.35/0.28	

Table S7. The ΔG of various reactions (eV) and η (V) for the OER and ORR process over bare and hydroxylated $(HO)_2$-CoFe/DG.

Reactions	ΔG(eV)	η(V)
Co-Fe bridge center of CoFe/DG		
OH^-+*→OH*+e^-	–2.32	η^{OER}=1.95
OH^-+OH*→O*+H_2O+e^-	–0.28	
OH^-+O*→OOH*+e^-	1.85	η^{ORR}=2.72
OH^-+OOH*→*+O_2+H_2O+e^-	2.35	
Co center / Co-Fe bridge center / Fe center of $(HO)_2$-CoFe/DG		

OH^{-}+*→OH*+e^{-}	0.29/0.37/–0.15	η^{OER}=0.50/1.16/0.73
OH^{-}+OH*→O*+H_2O+e^{-}	0.37/–0.45/0.02	
OH^{-}+O*→OOH*+e^{-}	0.90/1.56/1.13	η^{ORR}=0.36/0.85/0.55
OH^{-}+OOH*→*+O_2+H_2O+e^{-}	0.04/0.13/0.60	

Table S8. The ΔG of various reactions (eV) and η (V) for the OER and ORR process over bare and hydroxylated $(HO)_2$-NiFe/DG.

Reactions	ΔG(eV)	η(V)
	Ni-Fe bridge center of NiFe/DG	
OH^{-}+*→OH*+e^{-}	–0.79	η^{OER}=1.21
OH^{-}+OH*→O*+H_2O+e^{-}	–0.07	
OH^{-}+O*→OOH*+e^{-}	1.62	η^{ORR}=1.19
OH^{-}+OOH*→*+O_2+H_2O+e^{-}	0.86	
	Ni center / Ni-Fe bridge center / Fe center of $(HO)_2$-NiFe/DG	
OH^{-}+*→OH*+e^{-}	0.48/0.19/–0.78	η^{OER}=0.59/0.70/1.19
OH^{-}+OH*→O*+H_2O+e^{-}	0.99/–0.27/–0.34	
OH^{-}+O*→OOH*+e^{-}	0.05/1.10/1.17	η^{ORR}=0.35/0.69/1.16
OH^{-}+OOH*→*+O_2+H_2O+e^{-}	0.08/0.58/1.56	

Table S9. Zero point energy corrections (ZPE) and entropic contributions (TS) and total energies (E) to the free Energies.

Species	ZPE (eV)	TS (eV)	E (eV)
H_2	0.27	0.41	–6.76
H_2O	0.56	0.67	–14.22
	M/DG / MM/DG / M^1M^2/DG		
OH*	0.33	0.08	–
O*	0.08	0.05	–
OOH*	0.39	0.16	–
O_2*	0.14	0.15	–
	HO-M/DG / HO-NiNi/DG		
HO-M/DG	0.33	0.08	–
OH*	0.73	0.17	–
O*	0.42	0.20	–
OOH*	0.82	0.25	–
O_2*	0.49	0.26	–
	$(HO)_2$-MM/DG / $(HO)_2$-M^1M^2/DG		
$(HO)_2$-M^1M^2/DG	0.69	0.25	–
OH*	1.10	0.24	–
O*	0.80	0.25	–

OOH*	1.15	0.34	–
O_2*	0.87	0.31	–