Supporting Information

Theoretical insights on the catalytic activity and mechanism for oxygen reduction reaction at Fe and P codoped graphene

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Fig. S1 Various optimized configurations (top view) of Fe– P_x –G (x=1–4) and the corresponding formation energies. In the figure, the gray, pink and purple balls represent C, P and Fe atoms, respectively.



Fig. S2 Various optimized configurations (top view) of $\text{Fe}-P_x$ -zig-G (x=1-4) and the corresponding formation energies. In the figure, the gray, pink and purple balls represent C, P and Fe atoms, respectively.



Fig. S3 Various optimized configurations (top view) of $\text{Fe}-P_x$ -arm-G (x=1-4) and the corresponding formation energies. In the figure, the gray, pink and purple balls represent C, P and Fe atoms, respectively.

1. Free Energy Correction

The zero point energy correction is calculated as follows:

$$ZPE = \frac{1}{2} \sum_{i} hv_i$$

The entropy correction is calculated as follows [1]:

$$-TS = K_B T \sum_{i} \ln(1 - e^{-\frac{hv_i}{K_B T}}) - \sum_{i} hv_i(\frac{1}{e^{\frac{hv_i}{K_B T}}}) - K_B T$$

The enthalpic temperature correction is calculated as follows [1]:

$$\int C_p d_T = \sum_i h v_i \frac{1}{(e^{\frac{h v_i}{K_B T}} - 1)} + K_B T$$

where v is vibrational frequency and *i* represent the different modes of vibration for the intermediates. Each correction on the Fe–P₂–zig–G catalyst is shown in Table S1.

References

[1] Leah Isseroff Bendavid and Emily A. Carter, J. Phys. Chem. C, 2013, 117, 26048-26059

Table S1 The free energy correction (eV) from zero point energy, enthalpic temperature (at 298.15 K and 1 atm) and entropic contributions for the energy barriers ΔE_1 (eV) and reaction energies ΔE_2 (eV) of each elementary reaction for oxygen reduction on the Fe-P₂-zig-G catalyst.

		ΔE_1				ΔE_2			
	ΔE_{DFT}	ΔZPE	$\Delta \int C_P d_T$	$-T\Delta S$	ΔE_{DFT}	ΔZPE	$\Delta \int C_P d_T$	$-T\Delta S$	
$*O_2 \rightarrow *O +*O$	0.75	-0.04	-0.01	0.00	-1.71	0.01	0.00	0.02	
$*O_2 + *H \rightarrow *OOH$	0.47	-0.08	-0.01	0.05	-0.33	0.07	0.01	-0.03	
*OOH→*O+*OH	0.04	0.00	-0.02	0.07	-2.26	-0.03	0.00	0.04	
$OOH + H \rightarrow O + H_2O$	0.04	-0.03	-0.01	0.03	-2.38	0.06	0.01	-0.01	
$OOH + H \rightarrow OH + OH$	0.17	-0.05	-0.01	0.00	-3.72	-0.04	0.02	-0.01	
*O +*H→*OH	0.30	-0.07	-0.02	0.06	-1.46	0.03	0.01	-0.02	
$*OH + *H \rightarrow *H_2O$	0.27	-0.10	-0.01	0.03	-0.53	0.09	0.02	-0.05	
$O + O + H \rightarrow O + O H$	0.36	-0.08	-0.01	0.03	-0.61	0.02	0.02	-0.04	
$O + OH + H \rightarrow O+ H_2O$	0.05	0.08	-0.01	0.02	0.01	0.09	0.01	-0.02	
$*O +*OH +*H \rightarrow *OH +*OH$	0.53	-0.07	-0.01	0.02	-1.28	0.05	0.01	-0.01	

$*OH+*OH+*H \rightarrow *OH+*H_2O$	0.14	-0.12	0.02	-0.02	-0.34	0.06	0.02	-0.02
$*H_2O \rightarrow H_2O$					0.32	-0.02	0.01	-0.03
$*O+*H_2O \rightarrow *O+H_2O$					0.46	-0.04	0.03	-0.08
$*OH+*H_2O \rightarrow *OH+H_2O$	0.47	-0.04	0.01	-0.06	0.32	-0.02	0.02	-0.12

2. Computational Hydrogen Electrode

The computational hydrogen electrode (CHE) model is introduced by Nørskov and co-workers [2]. The free energy changes as a linear function of the electrode potential (U) [3]:

$$\Delta G(U) = \Delta G(U = 0) + eU = \Delta E_{DFT} + \Delta E_{ZPE} + \Delta \int C_P dT - T\Delta S + eU$$

where ΔE_{DFT} is the total energy change obtained from DFT calculations, ΔE_{ZFE} is the change in zero-point energy, *T* is the temperature (298.15 K), ΔS is the change in entropy, *e* is the charge transferred, *U* is the electrode potential with respect to the standard hydrogen electrode (defined at pH=0) and it is converted to the reversible hydrogen electrode (RHE) by subtracting kT ×pH× ln 10 in which pH=0 for acid medium. The entropies of H₂(g) are calculated at 1 atm, while the entropy of H₂O(g=l) is calculated at 0.035 atm, where the gas-phase H₂O is in equilibrium with the liquid H₂O. The free energy of O₂(g) is calculated according to G₀₂=2G_{H20}-2G_{H2}+4.92. The free energy diagrams of ORR via the two competing reaction pathways at the potential of U=0.00 V and U=1.23 V on the Fe-P₂-zig-G catalyst are shown in Fig. S4.

[2] Nørskov, J. K. K.; Rossmeisl, J.; Logadottir, A.; Lindqvist, L.; Kitchin, J. R.; Bligaard, T.; Jónsson, H.; Norskov, J. K.; Jonsson, H. Origin of the Overpotential for Oxygen Reduction at a Fuel-cell Cathode. *J. Phys. Chem. B* 2004, 108, 17886-17892.
[3] A.A. Peterson, F. Abild-Pedersen, F. Studt, J. Rossmeisl, J.K. Nørskov, Energ. Environ. Sci. 3 (2010) 1311-1315.



Fig. S4. Atomic differential charge density distributions with the same level of isosurfaces of the (a) $Fe-P_2-zig-G$, (b) $Fe-P_4-G$, (c) $Fe-P_2-arm-G$, and (d) $Fe-P_2-G$. Yellow and blue denote the deletion and aggregation of electron, respectively. The brown, violet and golden balls denote C, P and Fe, respectively. The values denote the lost electron of Fe atom.