Supplementary Material

Density Functional Theory Study of Iron Phthalocyanine Porous Layer Deposited on Graphene Substrate: A Pt-Free Electrocatalyst for Hydrogen Fuel Cells

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The relative free energies were calculated using the following equation:

$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S$

Where, E is the electronic total energy in gas phase of all the species present in a given reaction step, E_{ZPE} is the zero point energy and TS is the entropy term.

The free energy change of a reaction with solvation energy correction is given by the following equation:

$\Delta G_{sol} = \Delta E_{sol} + \Delta E_{ZPE(sol)} - T\Delta S_{sol}$

Where, E_{sol} is the electronic total energy with solvation energy correction to gas phase energy of all the species present in a given reaction step, $E_{ZPE(sol)}$ is the zero point energy and TS_{sol} is the entropy term with solvation energy correction.

Table S1. Free energy of reaction pathway-1 at 300 K with two different electrode potentials at pH = 0 of each ORR elementary step for the complete dissociative mechanism.

	ΔG	ΔG_{sol}	ΔG	ΔG_{sol}
Reaction	***V= 0 volt***		***V = 1.23 volt***	
$O_2 \rightarrow O_2$* (chemisorbed)	-0.61	-0.70	-0.61	-0.70
O_2* (chemisorbed) → O−O (TS)	2.55	2.70	2.55	2.70
O−O (TS) → O* + *O	-2.50	-2.96	-2.50	-2.96
O* + *O → HO* + *O	-0.98	-0.40	0.25	0.83
HO* + *O → H_2O + *O	-0.82	-1.03	0.41	0.20
H_2O + *O → H_2O + *OH	0.17	-0.10	1.40	1.13
H_2O + *OH → $2H_2O$	-2.72	-2.44	-1.49	-1.21

Table S2. Free energy of reaction pathway-2 at 300 K with two different electrode potentials at pH = 0 of each ORR elementary step for the complete dissociative mechanism.

	ΔG (ev)	ΔG_{sol} (ev)	ΔG (ev)	ΔG_{sol} (ev)
Reaction	***V= 0 volt***		***V = 1.23 volt***	
$O_2 \rightarrow O_2$* (chemisorbed)	-0.61	-0.70	-0.61	-0.70
O_2* (chemisorbed) → O−O (TS)	2.55	2.70	2.55	2.70
O−O (TS) → O* + *O	-2.50	-2.96	-2.50	-2.96
O* + *O → HO* + *O	-0.98	-0.40	0.25	0.83
HO* + *O → HO* + *OH	0.25	-0.16	1.48	1.07
HO* + *OH → H_2O + *OH	-0.91	-0.96	0.32	0.27
H_2O + *OH → $2H_2O$	-2.72	-2.44	-1.49	-1.21

Table S3. Free energy of reaction pathway-3 at 300 K with two different electrode potentials at pH = 0 of each ORR elementary step for the complete dissociative mechanism.

	ΔG (ev)	ΔG_{sol} (ev)	ΔG (ev)	ΔG_{sol} (ev)
Reaction	***V= 0 volt***		***V = 1.23 volt***	
$O_2 \rightarrow O_2$* (chemisorbed)	-0.61	-0.70	-0.61	-0.70
O_2* (chemisorbed) → O−O (TS)	2.55	2.70	2.55	2.70
O−O (TS) → O* + *O	-2.50	-2.96	-2.50	-2.96
O* + *O → O* + *OH	0.22	0.44	1.45	1.67
O* + *OH → HO* + *OH	-0.95	-1.00	0.28	0.23
HO* + *OH → H_2O + *OH	-0.91	-0.96	0.32	0.27
H_2O + *OH → $2H_2O$	-2.72	-2.44	-1.49	-1.21

Table S4. Free energy of reaction pathway-4 at 300 K with two different electrode potentials at pH = 0 of each ORR elementary step for the complete dissociative mechanism.

	ΔG (ev)	ΔG_{sol} (ev)	ΔG (ev)	ΔG_{sol} (ev)
Reaction	***V= 0 volt***		***V = 1.23 volt***	
$O_2 \rightarrow O_2$* (chemisorbed)	-0.61	-0.70	-0.61	-0.70
O_2* (chemisorbed) → O−O (TS)	2.55	2.70	2.55	2.70
O−O (TS) → O* + *O	-2.50	-2.96	-2.50	-2.96
O* + *O → O* + *OH	0.22	0.44	1.45	1.67
O* + *OH → O* + H_2O	-2.81	-2.79	-1.58	-1.56
O* + H_2O → HO* + H_2O	-0.75	-0.79	0.48	0.44
HO* + H_2O → $2H_2O$	-1.02	-0.82	0.21	0.41

Table S5. Free energy of reaction pathway-5 at 300 K with two different electrode potentials at pH = 0 of each ORR elementary step for the complete dissociative mechanism.

	ΔG (ev)	ΔG_{sol} (ev)	ΔG (ev)	ΔG_{sol} (ev)
Reaction	***V= 0 volt***		***V = 1.23 volt***	
$O_2 \rightarrow O_2$* (chemisorbed)	-0.61	-0.70	-0.61	-0.70
O_2* (chemisorbed) → O−O (TS)	2.55	2.70	2.55	2.70
O−O (TS) → O* + *O	-2.50	-2.96	-2.50	-2.96
O* + *O → O* + *OH	0.22	0.44	1.45	1.67
O* + *OH → HO* + *OH	-0.95	-1.00	0.28	0.23
HO* + *OH → HO* + H_2O	-2.60	-2.58	-1.37	-1.35
HO* + $H_2O \rightarrow 2H_2O$	-1.02	-0.82	0.21	0.41

Table S6. Free energy of reaction pathway-6 at 300 K with two different electrode potentials at pH = 0 of each ORR elementary step for the complete dissociative mechanism.

	ΔG (ev)	ΔG_{sol} (ev)	ΔG (ev)	ΔG_{sol} (ev)
Reaction	***V= 0 volt***		***V = 1.23 volt***	
$O_2 \rightarrow O_2$* (chemisorbed)	-0.61	-0.70	-0.61	-0.70
O_2* (chemisorbed) → O−O (TS)	2.55	2.70	2.55	2.70
O−O (TS) → O* + *O	-2.50	-2.96	-2.50	-2.96
O* + *O → HO* + *O	-0.98	-0.40	0.25	0.83
HO* + *O → HO* + *OH	0.25	-0.16	1.48	1.07
HO* + *OH → HO* + H_2O	-2.60	-2.58	-1.37	-1.35
HO* + $H_2O \rightarrow 2H_2O$	-1.02	-0.82	0.21	0.41

Table S7. Reaction free energy at 300 K with two different electrode potentials at pH = 0 of each ORR elementary step for the complete associative mechanism.

	ΔG (ev)	ΔG_{sol} (ev)	ΔG (ev)	ΔG_{sol} (ev)
Reaction	***V= 0 volt***		***V = 1.23 volt***	
$O_2 \rightarrow O_2$* (chemisorbed)	-0.61	-0.70	-0.61	-0.70
O_2* (chemisorbed) → HO−O*	-0.47	-0.55	0.76	0.68
HO−O* → H_2O + O*	-2.08	-2.06	-0.85	-0.83
H_2O + O* → H_2O + HO*	-0.74	-0.79	0.49	0.44
H_2O + HO* → $2H_2O$	-1.02	-0.82	0.21	0.41

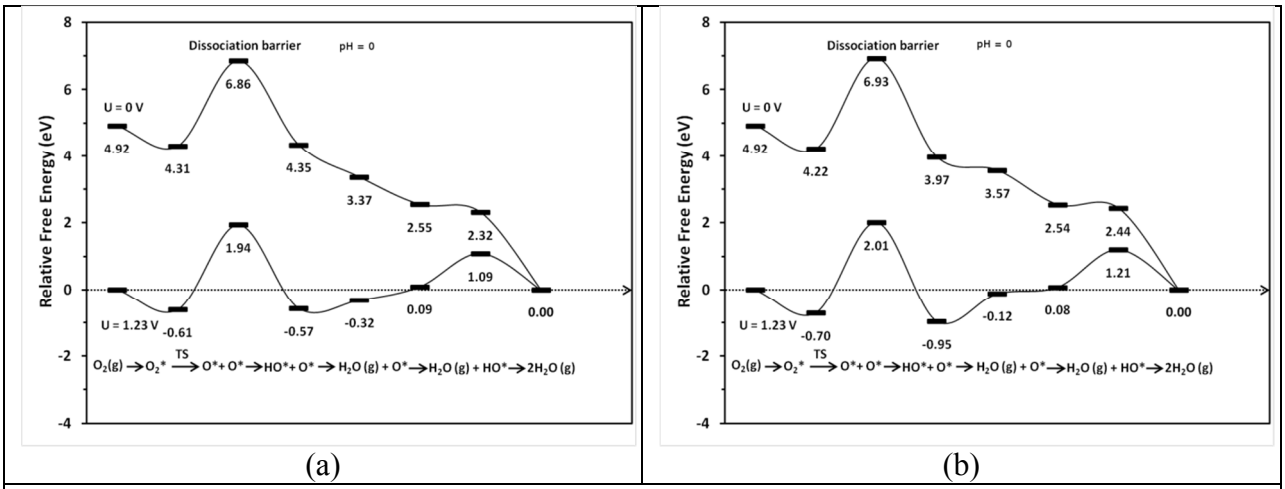
Table S8: Zero point energy corrections and entropic contributions to the free energies at T = 300K for dissociative mechanism.

	E_{ZPE} (eV)	ST (eV)	$E_{ZPE(sol)}$ (eV)	TS_{sol} (eV)
O_2* (chemisorbed)	0.08	1.15	0.07	1.09
O−O (TS)	0.06	1.15	0.06	1.14
O* + *O	0.08	0.85	0.08	1.11
O* + *OH	0.38	1.13	0.51	0.99
HO* + *O	0.34	1.12	0.46	0.98
HO* + *OH	0.65	1.14	0.76	0.99
HO*	0.34	0.93	0.36	0.95
*OH	0.43	0.95	0.44	0.94
O*	0.11	0.93	0.11	0.93
*O	0.13	0.92	0.13	0.92

Note: '*' after the O atom refers to metal site and '*' before O atom refers as N edge-site on FePc molecule.

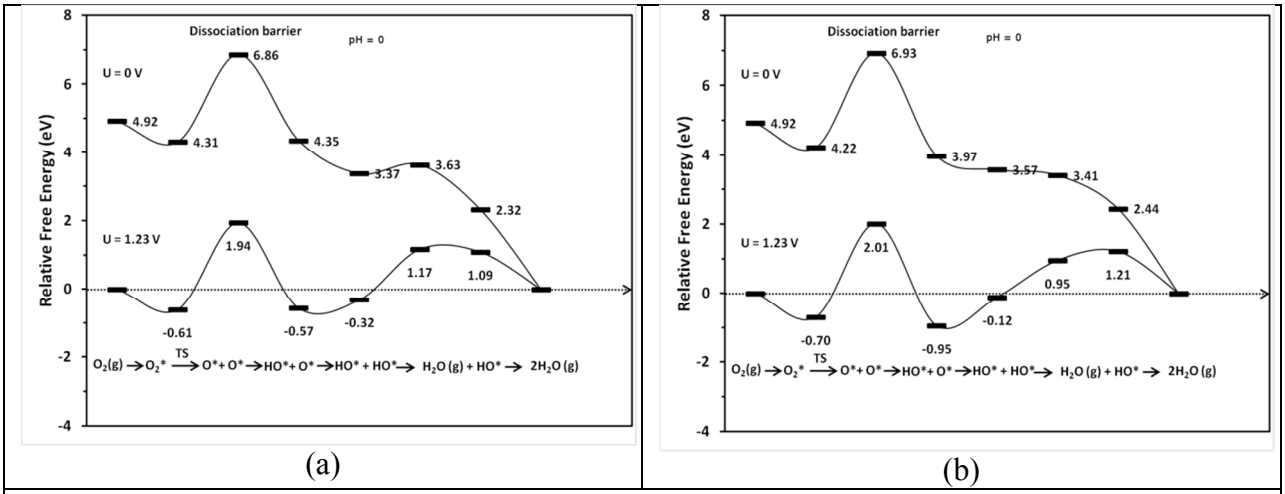
Table S9: Zero point energy corrections and entropic contributions to the free energies at T = 300K for associative mechanism

	E_{ZPE} (eV)	ST (eV)	$E_{ZPE(sol)}$ (eV)	TS_{sol} (eV)
O_2* (chemisorbed)	0.08	1.15	0.07	1.09
HO−O*	0.36	1.15	0.36	1.14
HO*	0.34	0.93	0.36	0.95
O*	0.11	0.93	0.11	0.93



(a) (b)

Figure S1. Electrocatalytic reaction free energy landscapes of ORR followed by complete WFR steps for the dissociative mechanism at two different potentials (a) without water solvation correction and (b) with water solvation model. The numbers indicate the energies relative to the reference system of two H_2O molecules on the FePc/graphene surface.



(a) (b)

Figure S2. Electrocatalytic reaction free energy landscapes of ORR followed by complete WFR steps for the dissociative mechanism at two different potentials (a) without water solvation correction and (b) with water solvation model. The numbers indicate the energies relative to the reference system of two H_2O molecules on the FePc/graphene surface.

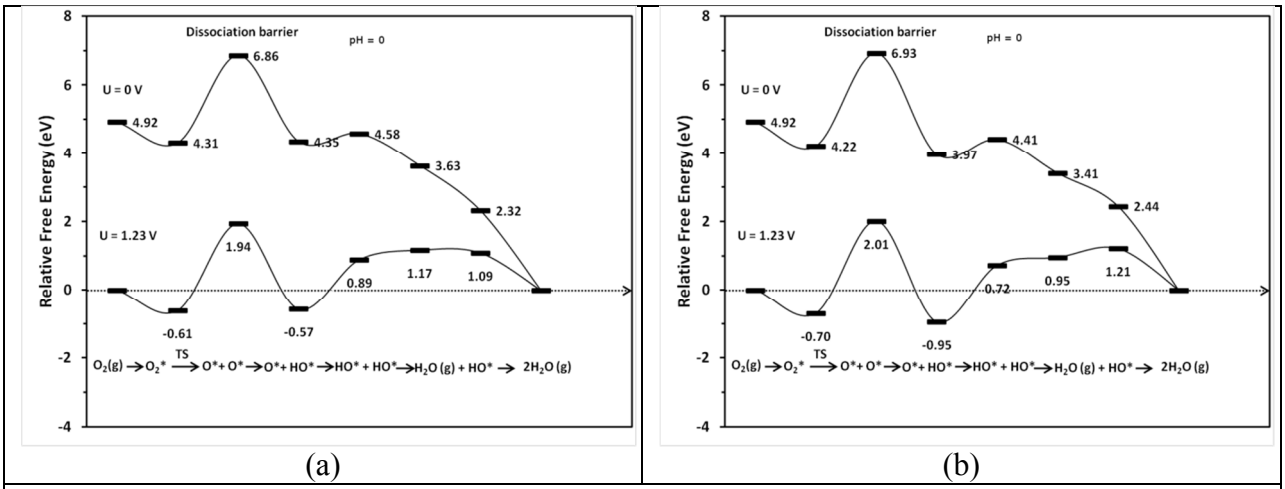


Figure S3. Electrocatalytic reaction free energy landscapes of ORR followed by complete WFR steps for the dissociative mechanism at two different potentials (a) without water solvation correction and (b) with water solvation model. The numbers indicate the energies relative to the reference system of two H_2O molecules on the FePc/graphene surface.

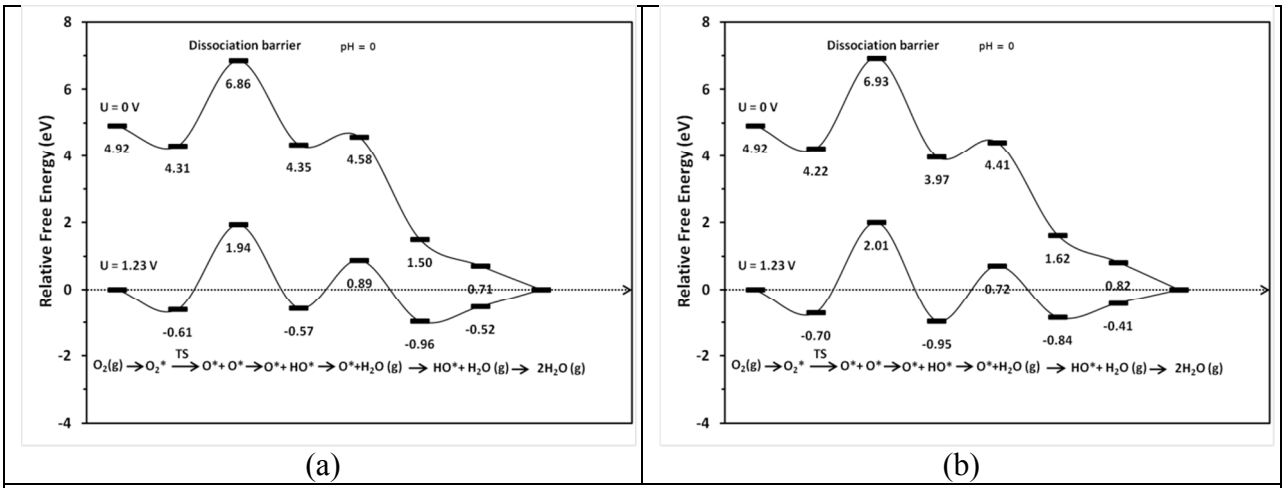


Figure S4. Electrocatalytic reaction free energy landscapes of ORR followed by complete WFR steps for the dissociative mechanism at two different potentials (a) without water solvation correction and (b) with water solvation model. The numbers indicate the energies relative to the reference system of two H_2O molecules on the FePc/graphene surface.

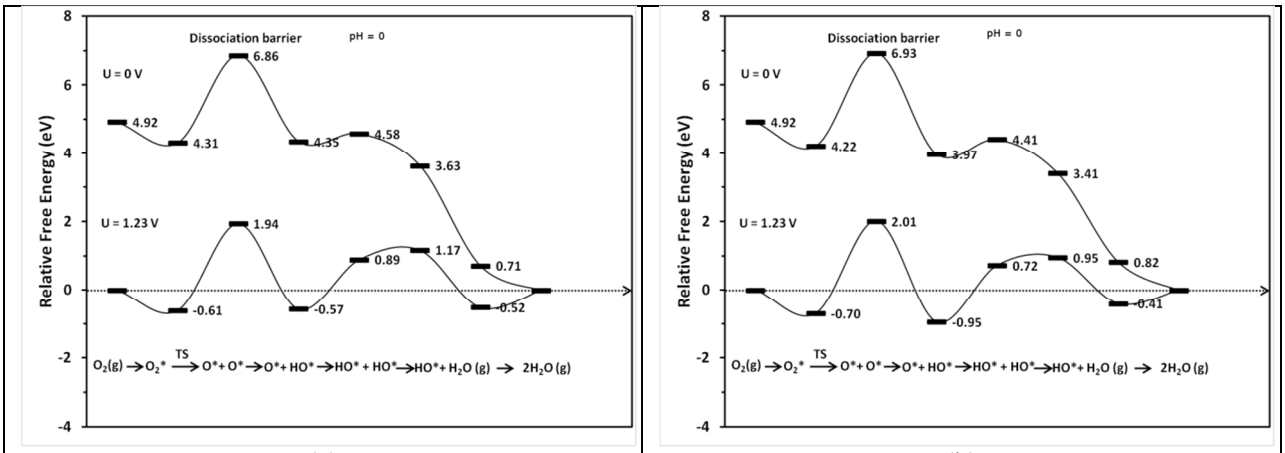


Figure S5. Electrocatalytic reaction free energy landscapes of ORR followed by complete WFR steps for the dissociative mechanism at two different potentials (a) without water solvation correction and (b) with water solvation model. The numbers indicate the energies relative to the reference system of two H_2O molecules on the FePc/graphene surface.

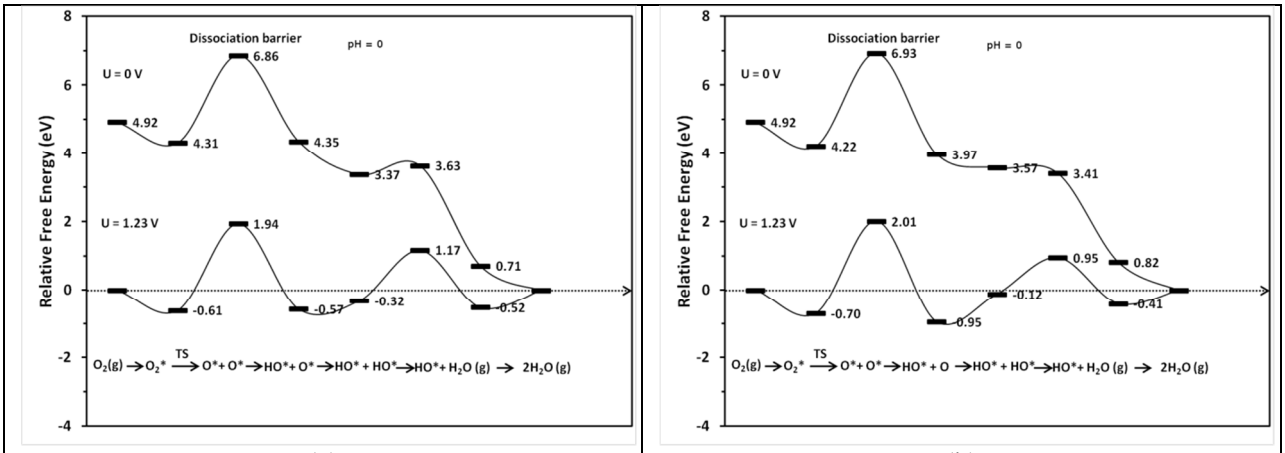


Figure S6. Electrocatalytic reaction free energy landscapes of ORR followed by complete WFR steps for the dissociative mechanism at two different potentials (a) without water solvation correction and (b) with water solvation model. The numbers indicate the energies relative to the reference system of two H_2O molecules on the FePc/graphene surface.