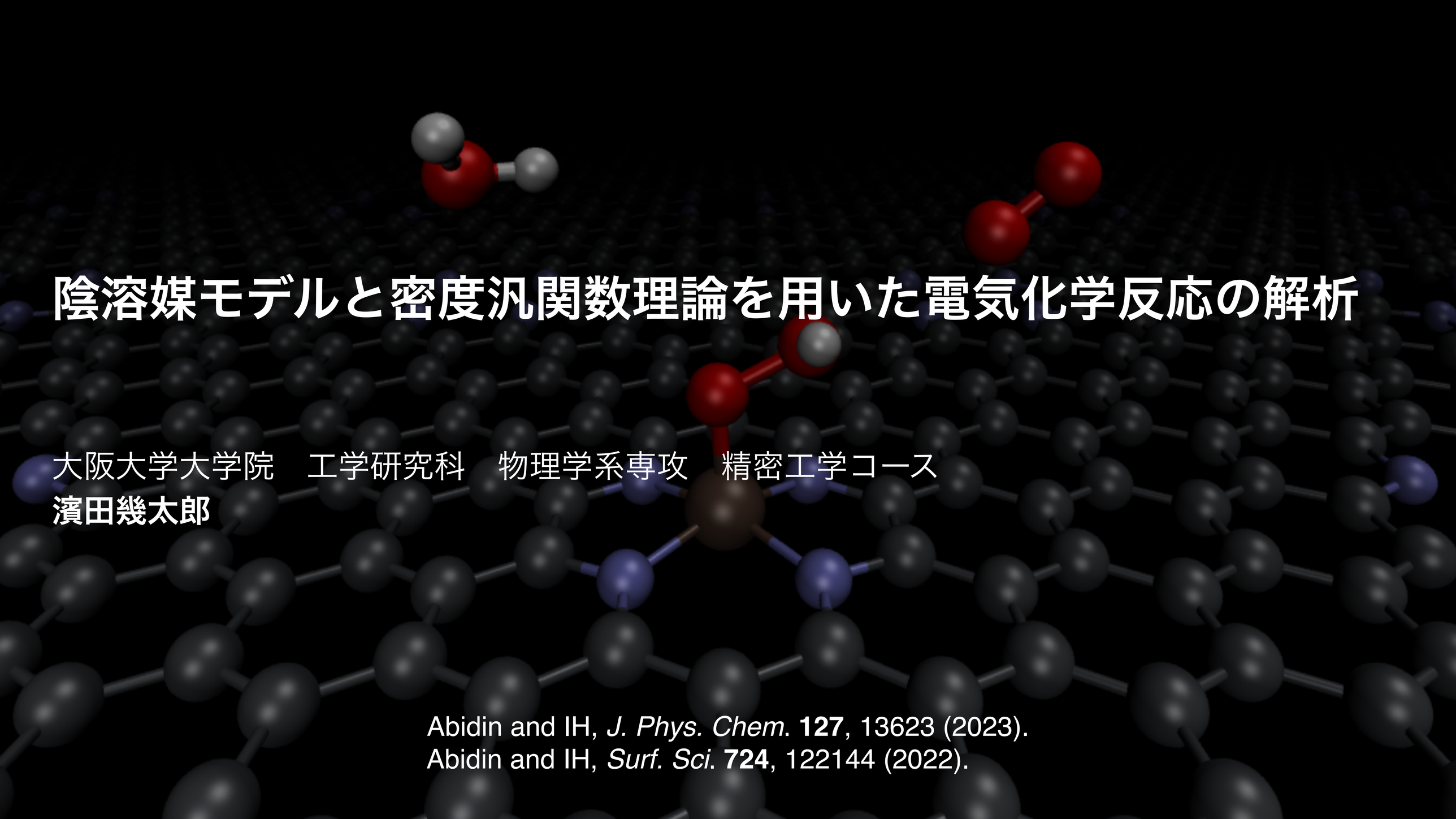

陰溶媒モデルと密度汎関数理論を用いた電気化学反応の解析

大阪大学大学院　工学研究科　物理学系専攻　精密工学コース
濱田幾太郎

Abidin and IH, *J. Phys. Chem*. **127**, 13623 (2023).
Abidin and IH, *Surf. Sci*. **724**, 122144 (2022).

Analysis of electrochemical reactions with density functional theory and implicit solvation model

Ikutaro Hamada
Department of Precision Engineering
Graduate School of Engineering
Osaka University

Abidin and IH, *J. Phys. Chem.* **127**, 13623 (2023).
Abidin and IH, *Surf. Sci.* **724**, 122144 (2022).

Azim Fitri Zainul Abidin
(The National University of Malaysia (UKM))

Proton exchange membrane fuel cell

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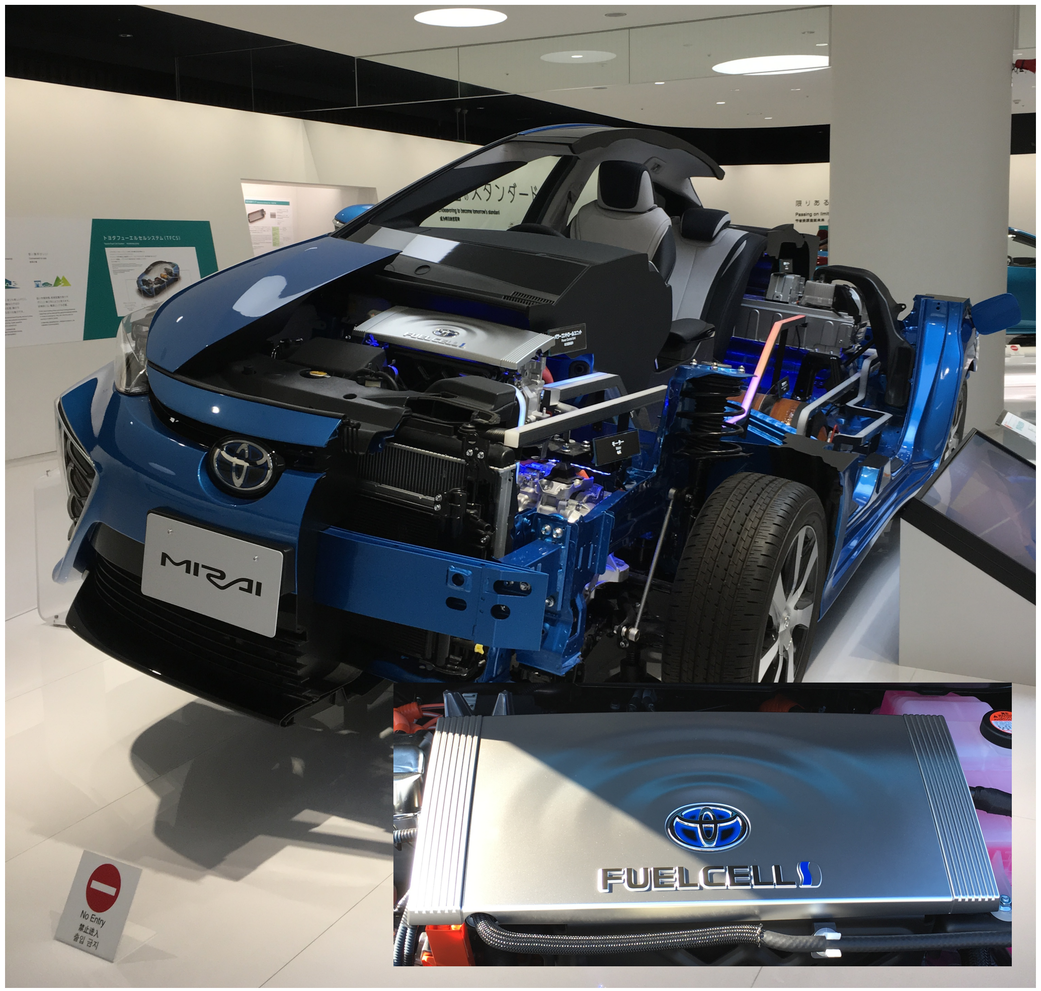

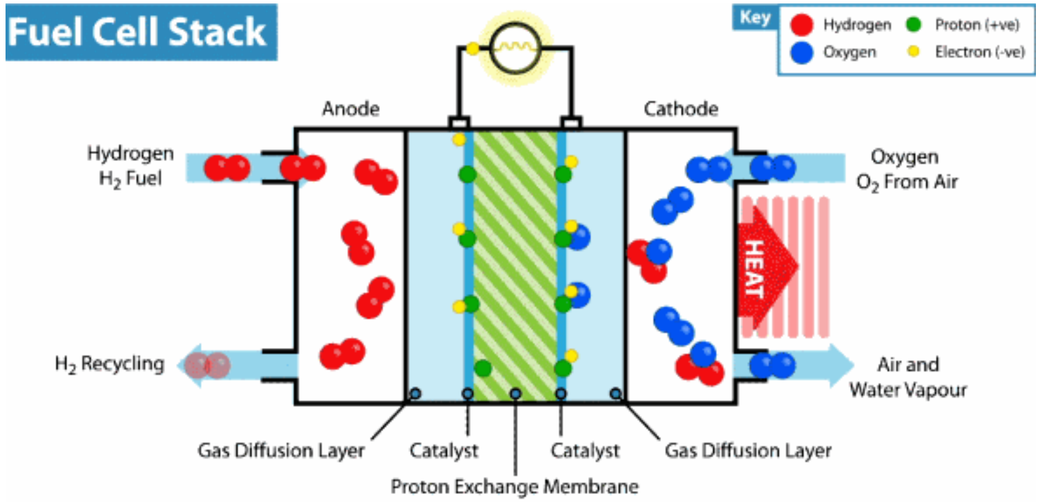

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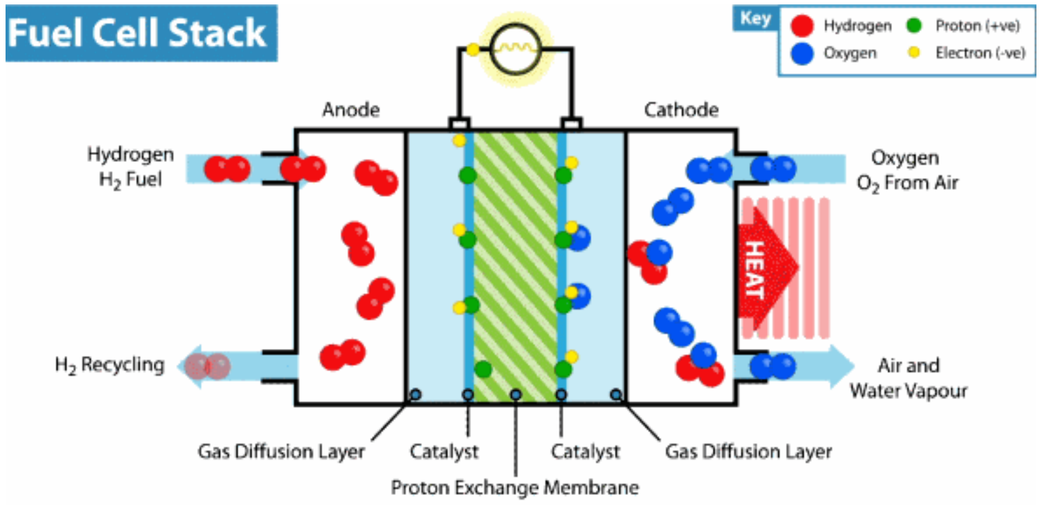

Anodic reaction (HOR)

$$H_2 \rightarrow 2H^+ + 2e^- \qquad E^o = 0 \text{ V}$$

Cathodic reaction (ORR)

$$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O \quad E^o = 1.23 \text{ V}$$

Overall reaction

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \qquad E^o = 1.23 \text{ V}$$

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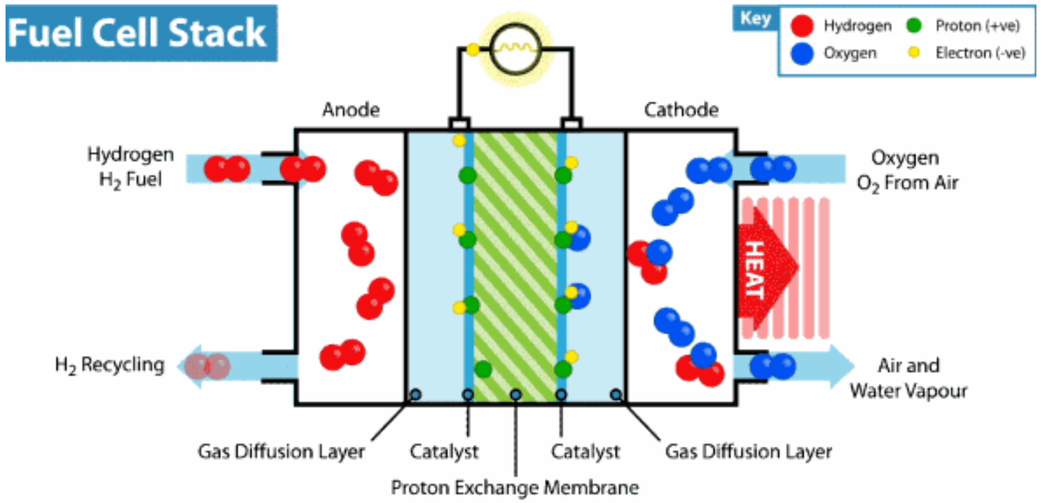

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☹ Sluggish cathodic oxygen reduction reaction (ORR)

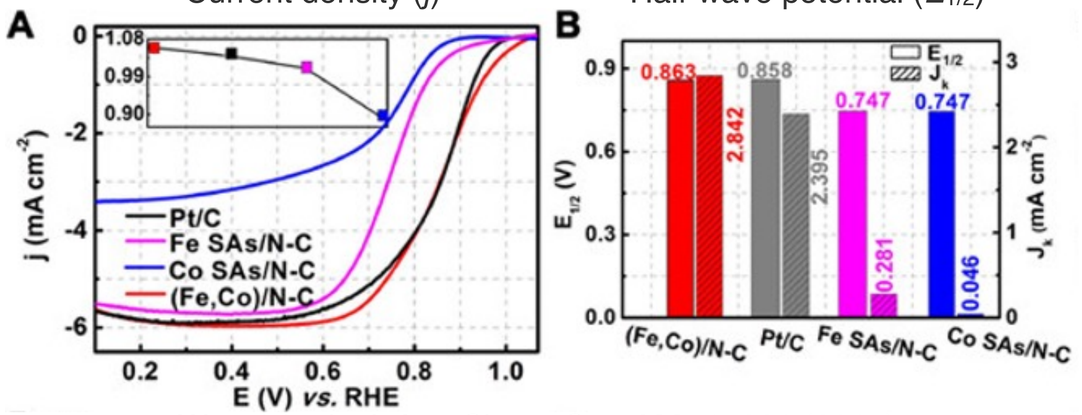
☹ Scarcity of the platinum group metals for catalyst

☛ Urgent need of alternative catalyst(s)

Transition metal single atom catalyst (TM-N-C, TM=Fe, Co) for ORR

Transition metal single atom catalyst (TM-N-C, TM=Fe, Co) for ORR

Current density (*j*) Half-wave potential ($E_{1/2}$)



Wang *et al., J. Am. Chem. Soc.* **139**, 17281 (2017).

Experimental $E_{1/2}$
Fe-N-C: 0.747 V
Co-N-C: 0.747 V
Pt/C : 0.858 V

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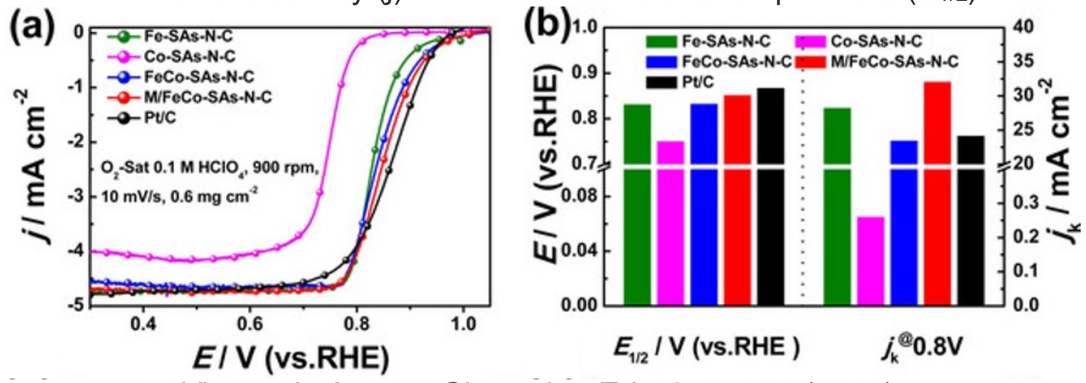

Yin *et al., Angew. Chem. Int. Ed.* **59**, 21976 (2020).

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Fe-N-C: 0.831 V
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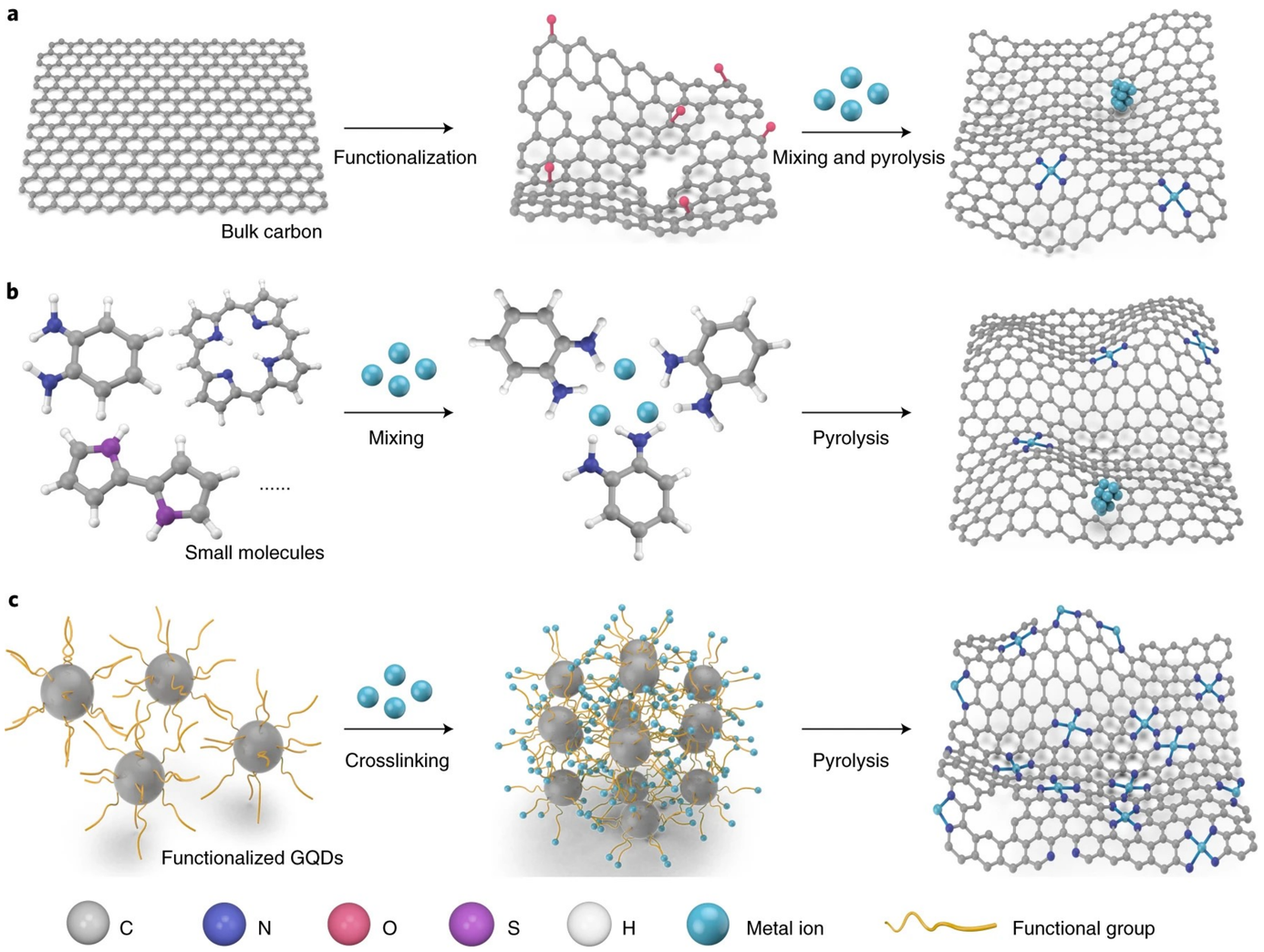
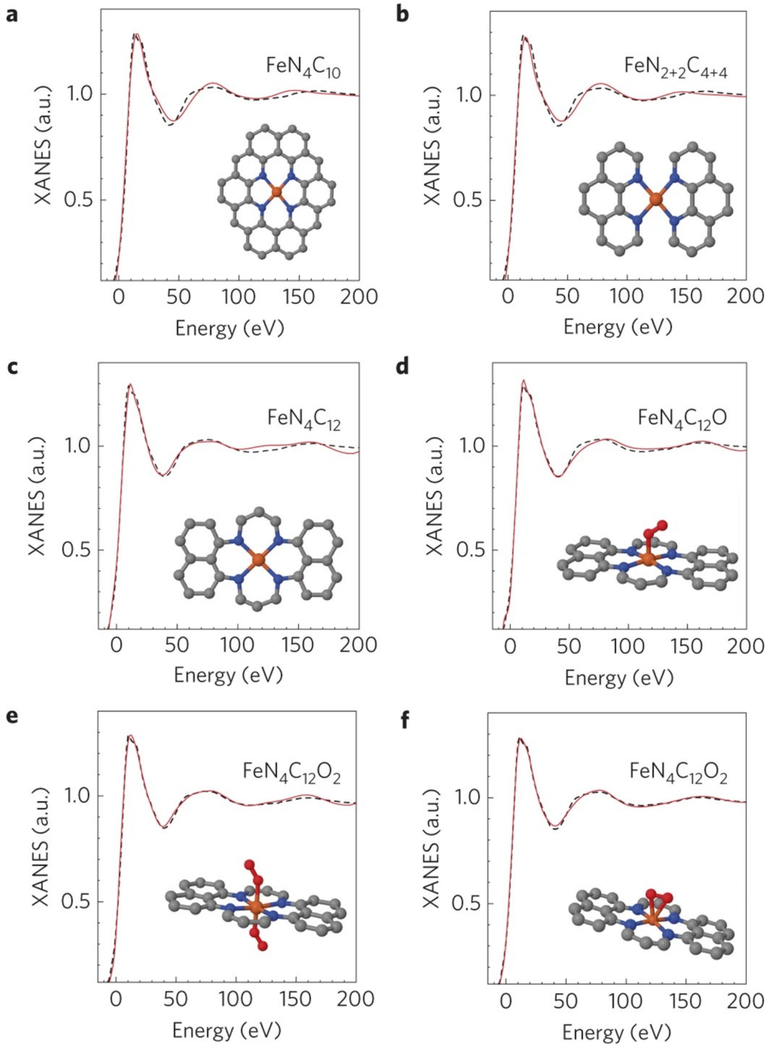
Pt/C : 0.867 V

Comparable performance of Fe-N-C and Co-N-C with Pt/C

TM-N_4-C moiety as an active site for ORR



Xia *et al., Nat. Chem.* **13**, 887 (2021).



Vitolo *et al., Nat. Mater.* **14**, 937 (2015).

Transition metal single atom catalyst (TM-N-C, TM=Fe, Co) for ORR

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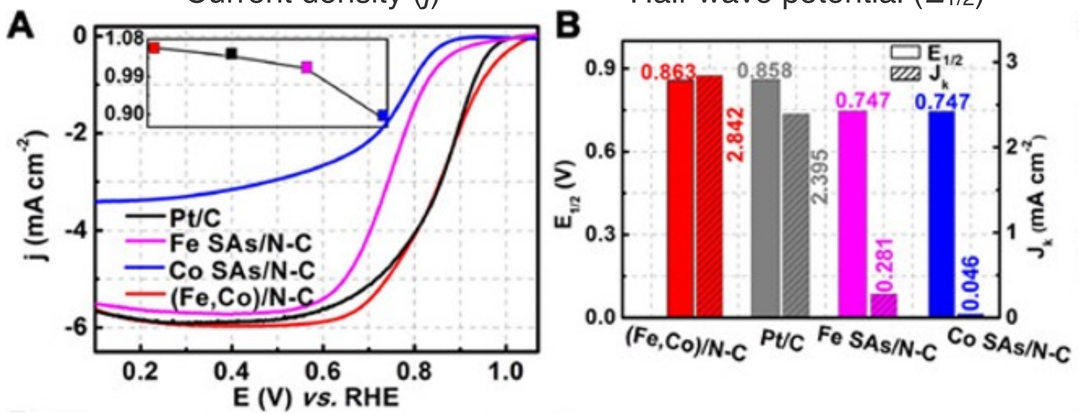

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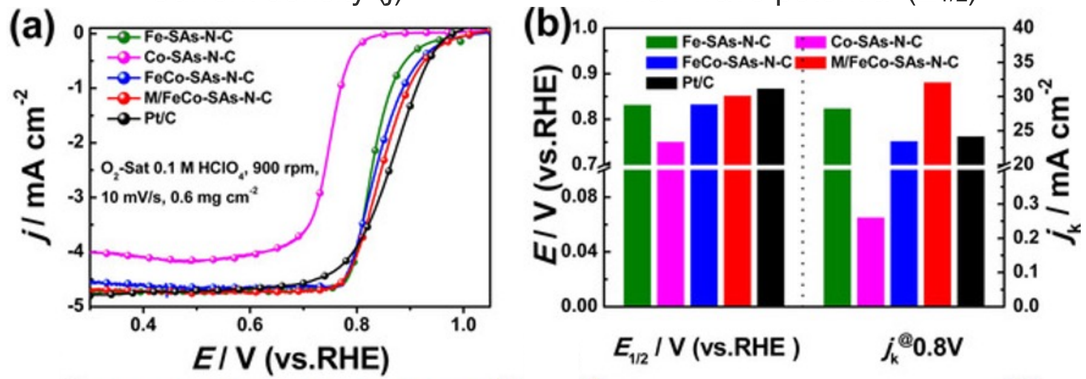

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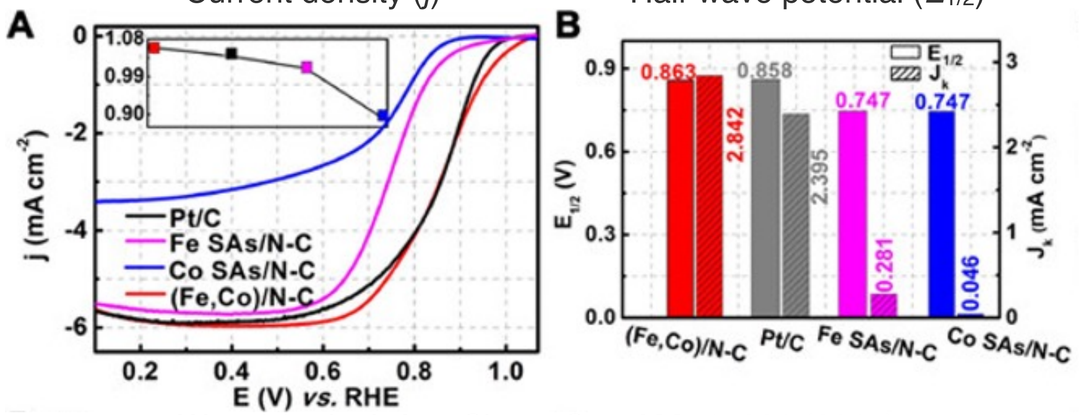

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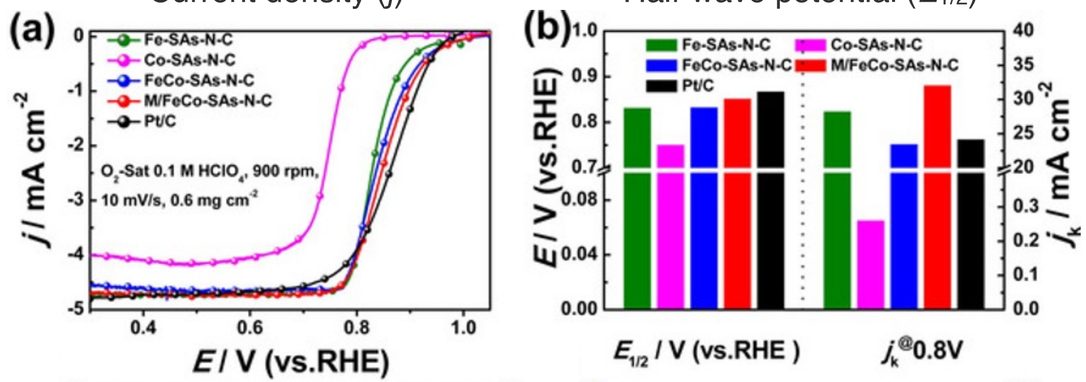

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DFT limiting potential (U_L)
Fe-N_4-C: 0.40 V
Co-N_4-C: 0.77 V
Pt(111) : 0.80 V

Patniboon and Hansen, *ACS Catal.* **11**, 13102 (2021).
Hansen *et al.*, *Phys. Chem. Chem. Phys.* **10**, 3722 (2008).

☹ DFT predicted limiting potential of Fe-N_4-C is underestimated
☹ DFT predicted limiting potentials of Fe-N_4-C and Co-N_4-C are *not* comparable

Possible problems and a solution in DFT calculation

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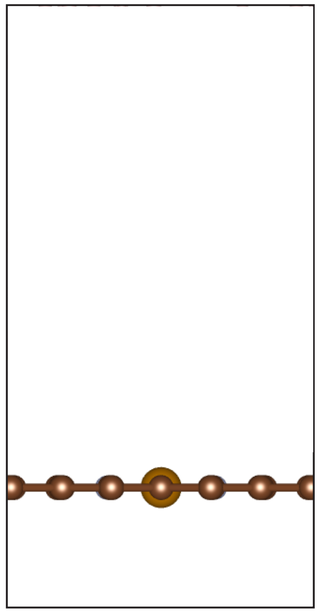
- Computational hydrogen electrode (CHE) model

Possible problems and a solution in DFT calculation

- Computational hydrogen electrode (CHE) model

  ☹ Vacuum environment

Simulation cell



Possible problems and a solution in DFT calculation

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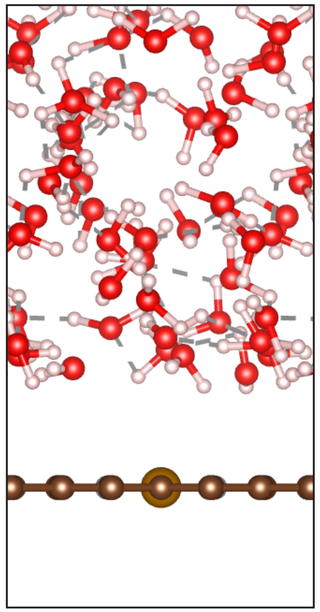
Explicit solvation model



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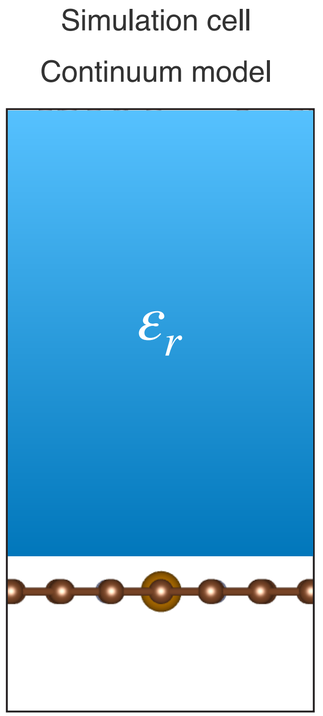

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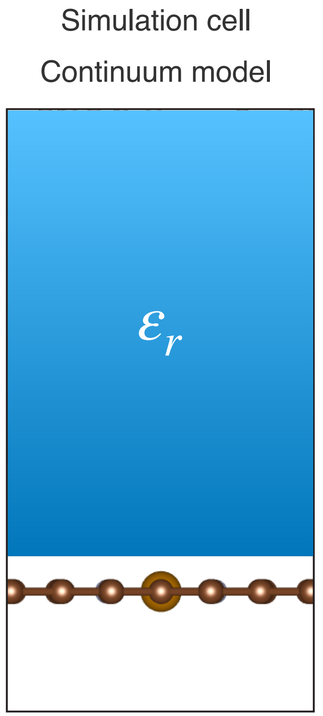
- **Effective screening medium**
  + reference interaction site model (ESM-RISM)



ESM-RISM: Nishihara & Otani, *Phys. Rev. B* **96**, 115429 (2017).

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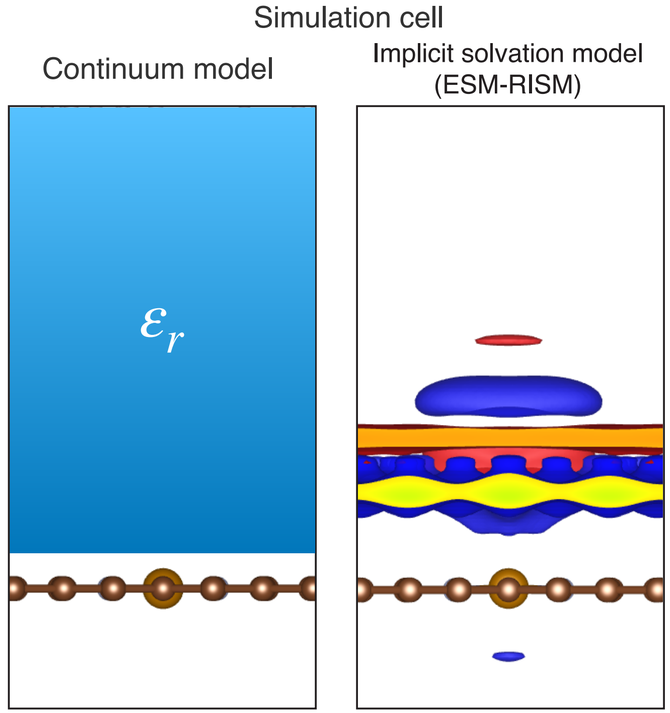

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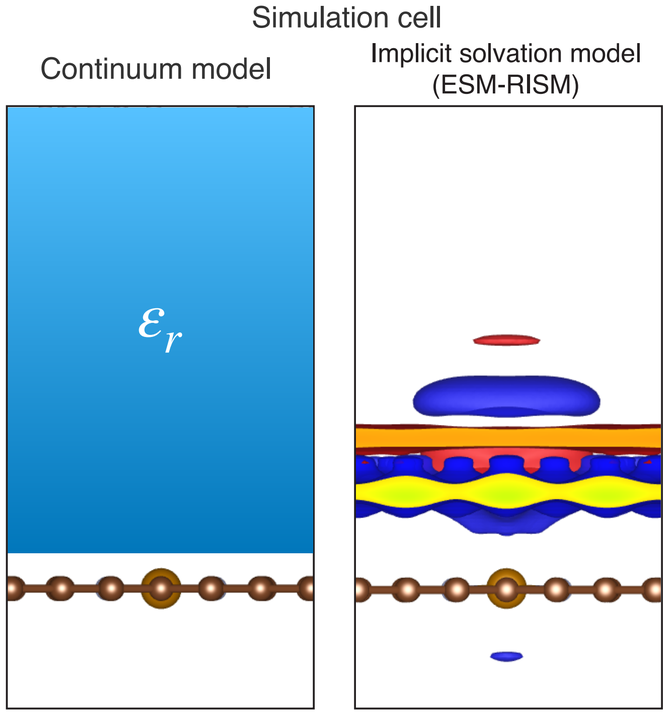

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Outline

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$$G_{\mathrm{H^+(aq)}}(U_{\mathrm{SHE}}) + \mu_{\mathrm{e}}(U_{\mathrm{SHE}}) = \frac{1}{2}G_{\mathrm{H_2(g)}} + \Delta G_{\mathrm{pH}} - |e|\,U_{\mathrm{SHE}}$$

pH correction

$$\Delta G_{\mathrm{pH}} = -\,k_{\mathrm{B}}T\ln[\mathrm{H^+}] = k_{\mathrm{B}}T\ln(10)\times \mathrm{pH}$$

Nørskov *et al.*, *J. Phys. Chem. B* **108**, 17886 (2004).

ORR mechanism on TM-N_4-C

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4-electron associative mechanism (in an acid electrolyte)

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

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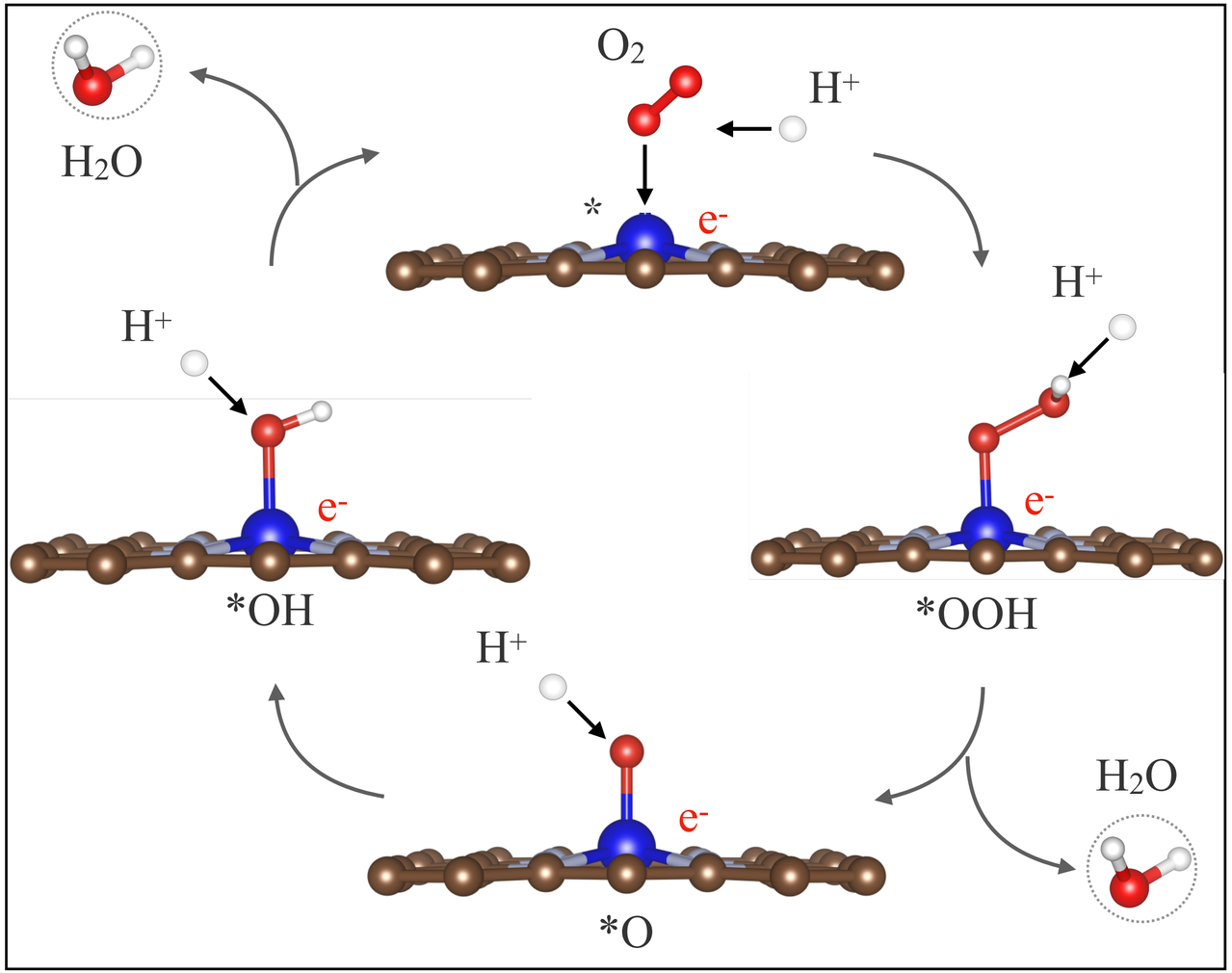
$$O_2 + H^+ + e^- + * \rightarrow * OOH$$

$$*OOH + H^+ + e^- \rightarrow *O + H_2O$$

$$*O + H^+ + e^- \rightarrow *OH$$

$$*OH + H^+ + e^- \rightarrow H_2O$$



ORR mechanism on TM-N_4-C

4-electron associative mechanism (in an acid electrolyte)

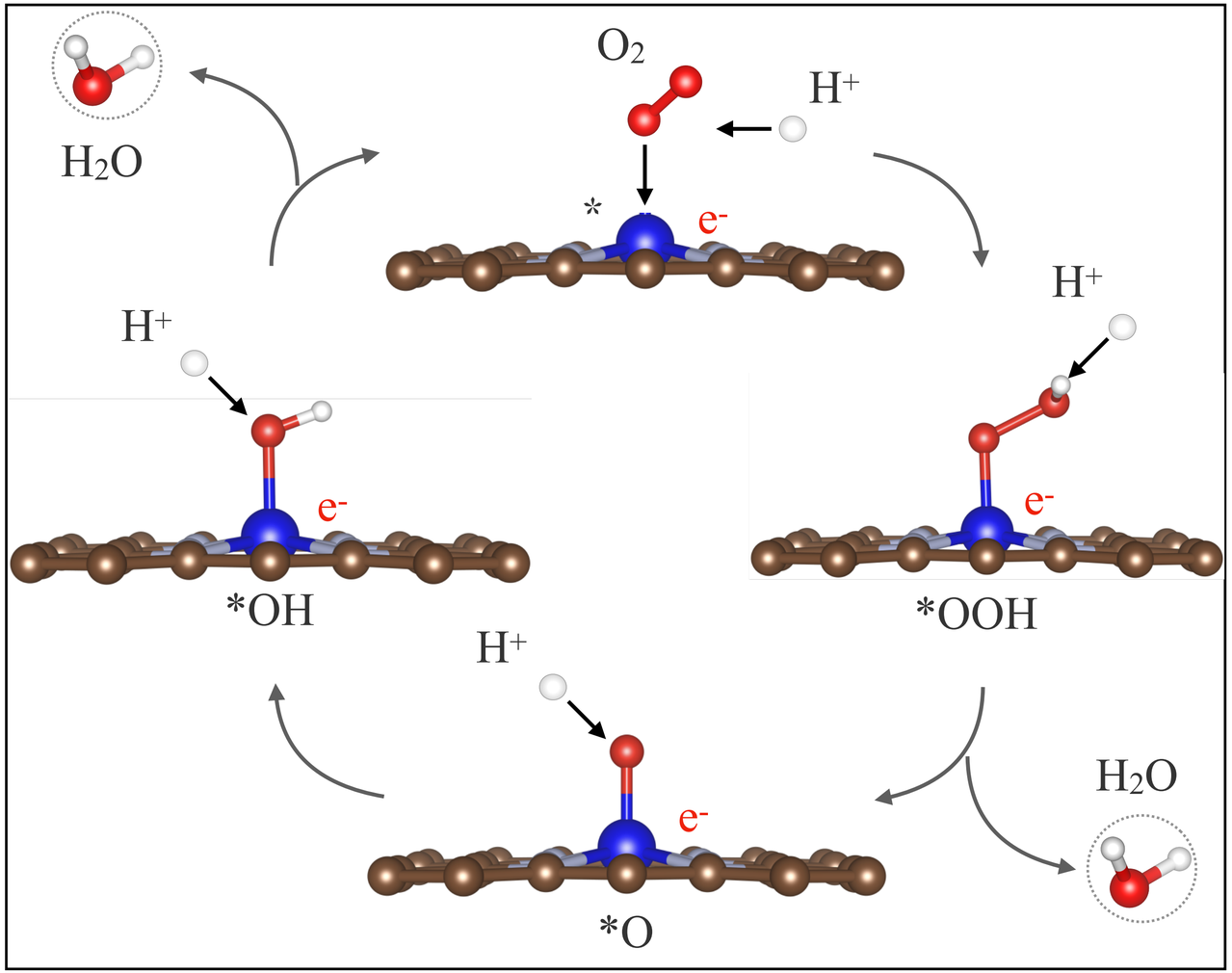
$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

$$O_2 + H^+ + e^- + * \rightarrow * OOH \quad \Delta G(*OOH)$$

$$*OOH + H^+ + e^- \rightarrow *O + H_2O \quad \Delta G(*O)$$

$$*O + H^+ + e^- \rightarrow *OH \quad \Delta G(*OH)$$

$$*OH + H^+ + e^- \rightarrow H_2O \quad \Delta G(H_2O)$$



Free energies of ORR intermediates

Free energies of ORR reactants and intermediates wrt the final state

$$\Delta G(\mathrm{O_2}) = -\Delta G_{\mathrm{ORR}} - 4\,|e|\,U_{\mathrm{RHE}}$$

$$\Delta G(*\mathrm{OOH}) = \Delta G(*\mathrm{OOH}, U_{\mathrm{RHE}} = 0) - 3\,|e|\,U_{\mathrm{RHE}}$$

$$\Delta G(*\mathrm{O}) = \Delta G(*\mathrm{O}, U_{\mathrm{RHE}} = 0) - 2\,|e|\,U_{\mathrm{RHE}}$$

$$\Delta G(*\mathrm{OH}) = \Delta G(*\mathrm{OH}, U_{\mathrm{RHE}} = 0) - |e|\,U_{\mathrm{RHE}}$$

$$\Delta G_{\mathrm{ORR}} = 2G(\mathrm{H_2O(l)}) - 2G(\mathrm{H_2(g)}) - G(\mathrm{O_2(g)}) = -1.23 \times 4\ \mathrm{V}$$

$$\Delta G(*\mathrm{OOH}) = G(\mathrm{OOH}) - G(*) - [2G(\mathrm{H_2O(l)}) - 3/2G(\mathrm{H_2})]$$

$$\ldots$$

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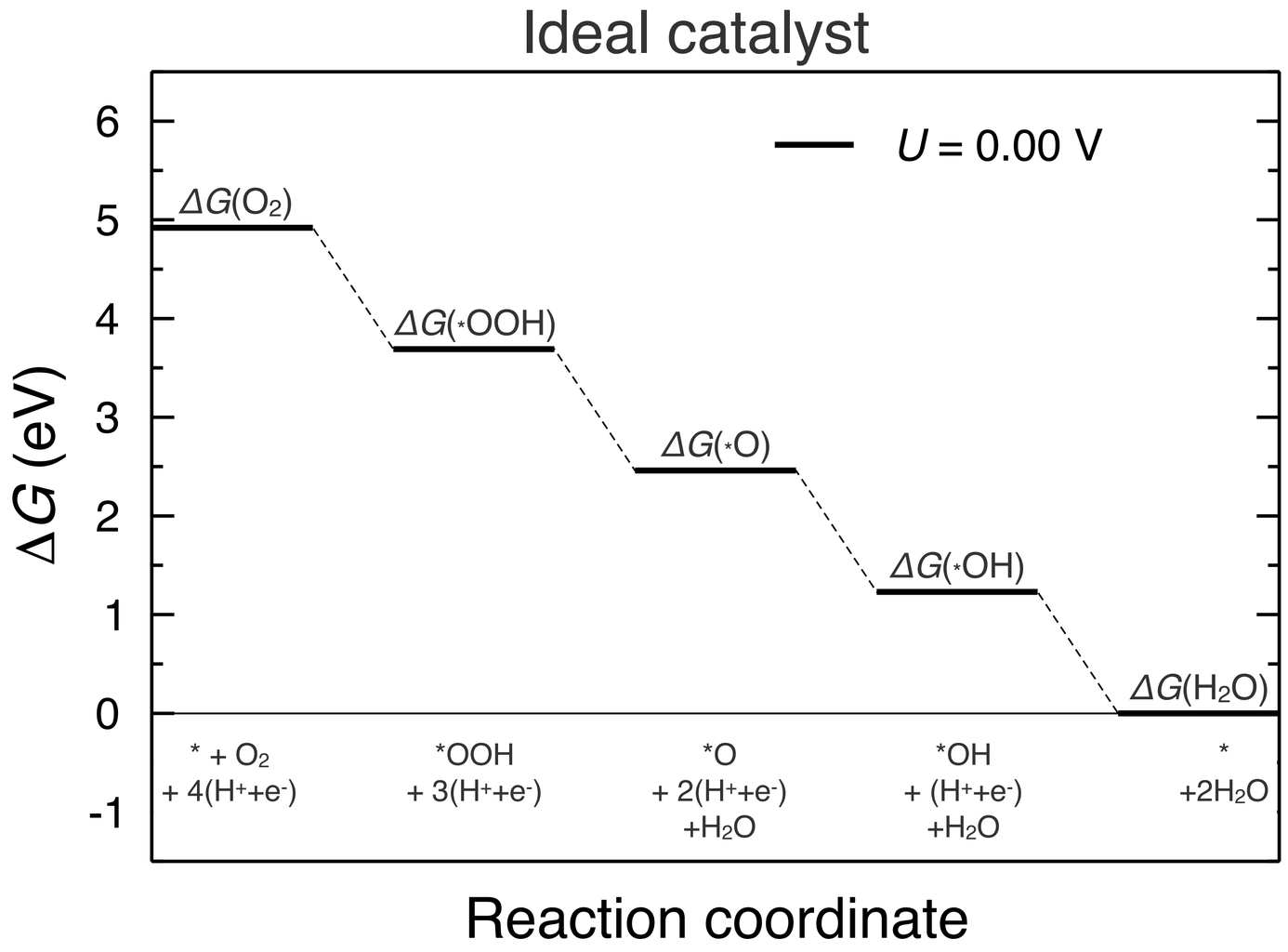
ORR mechanism



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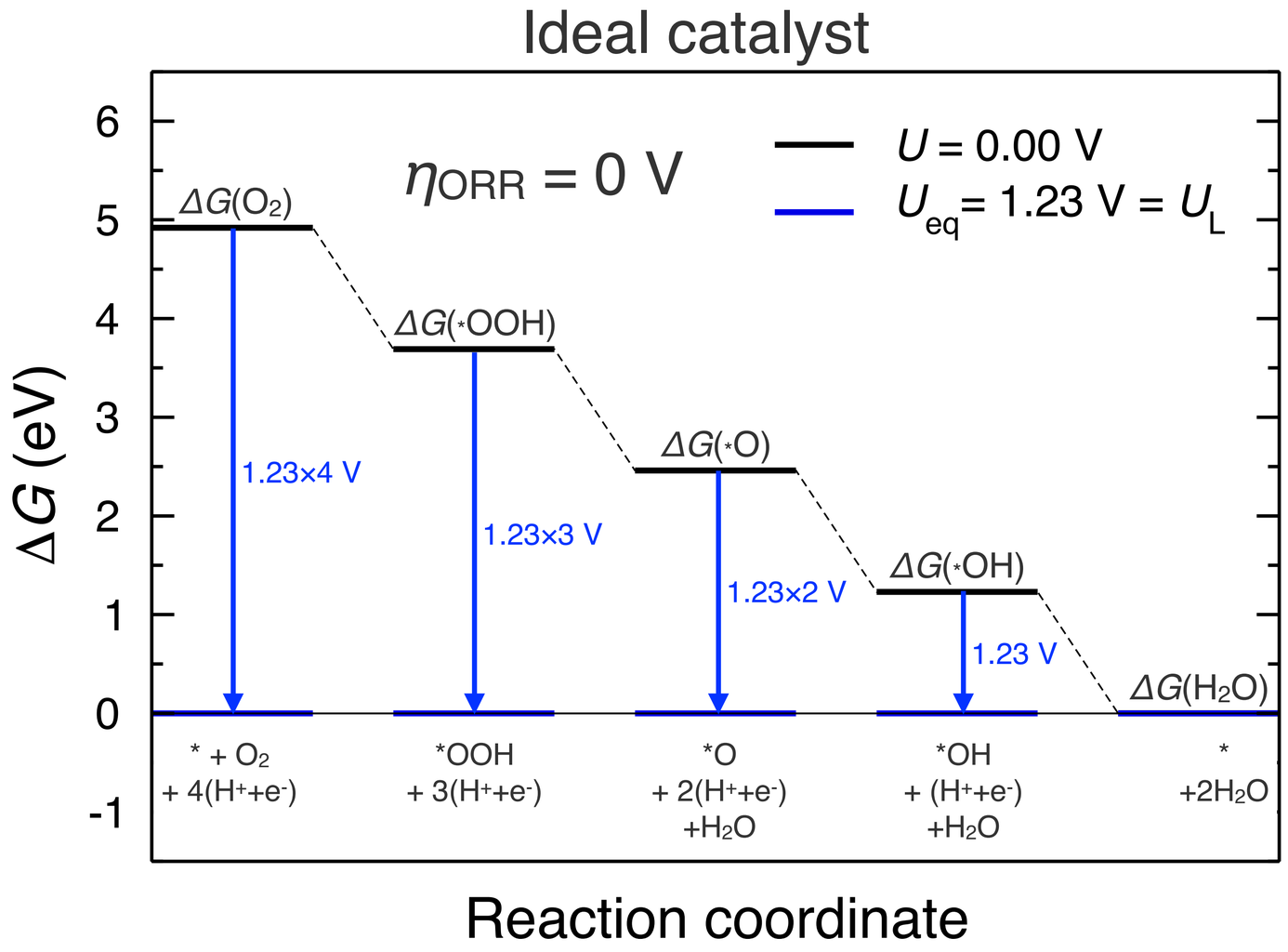

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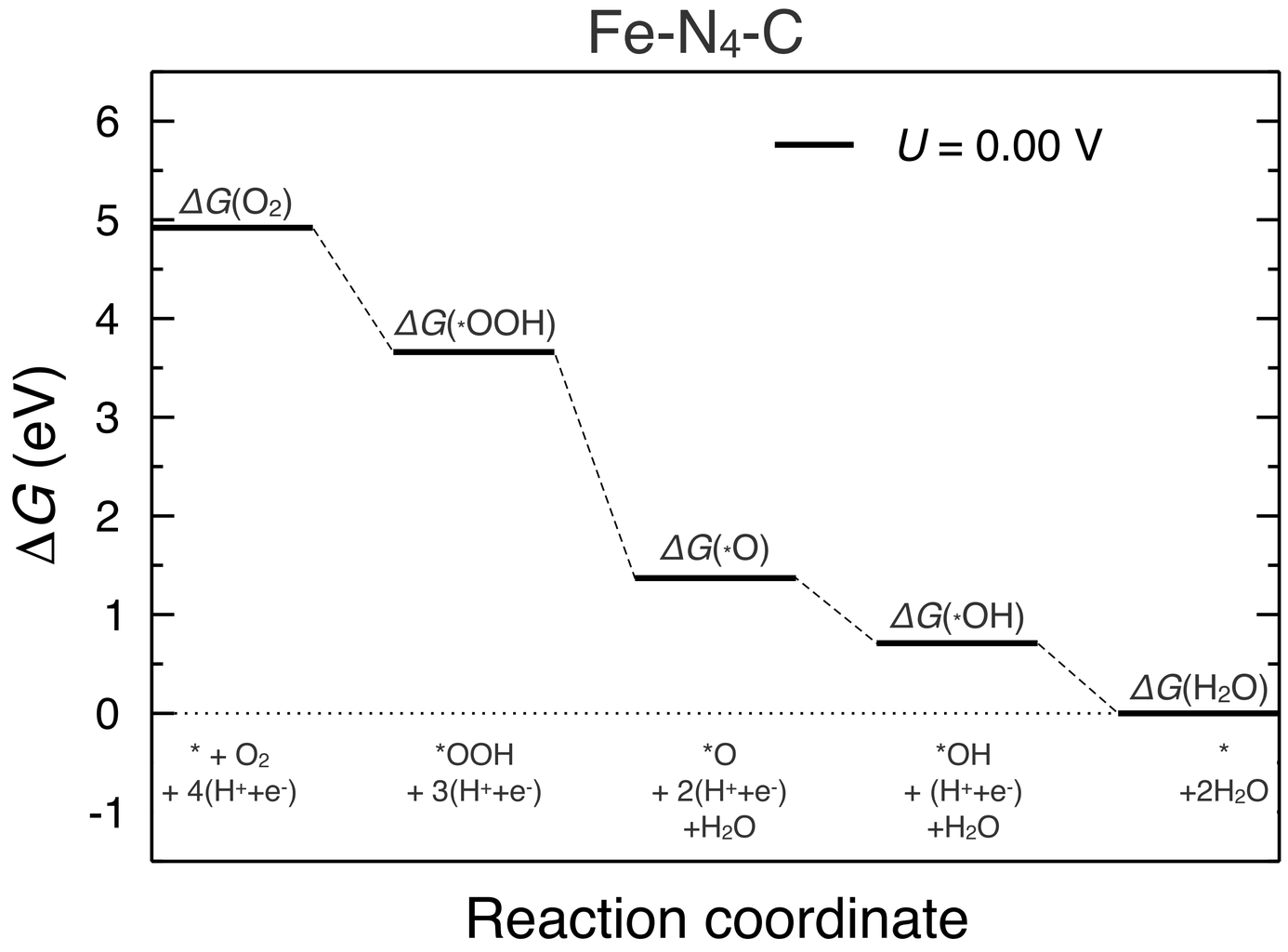

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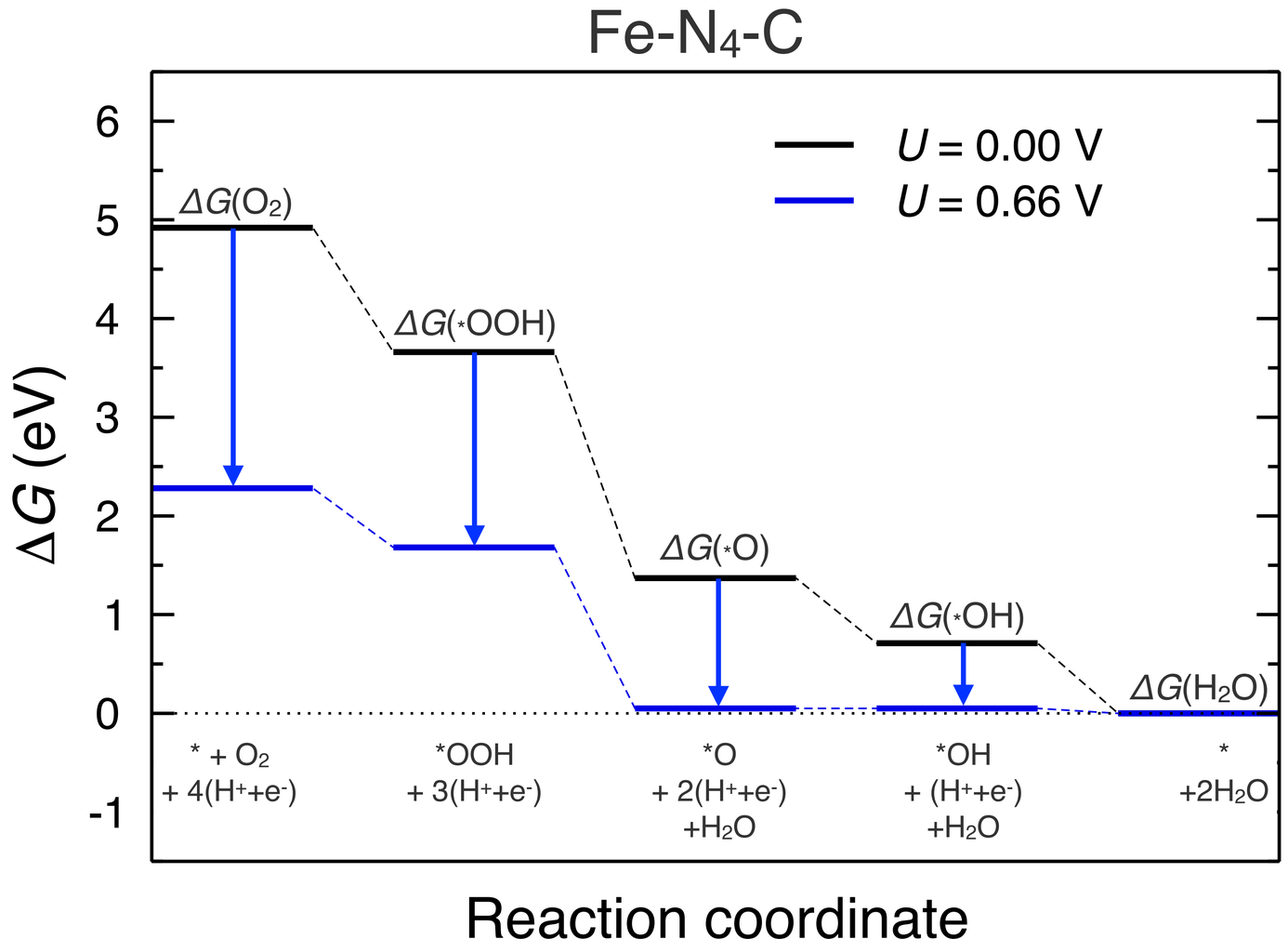

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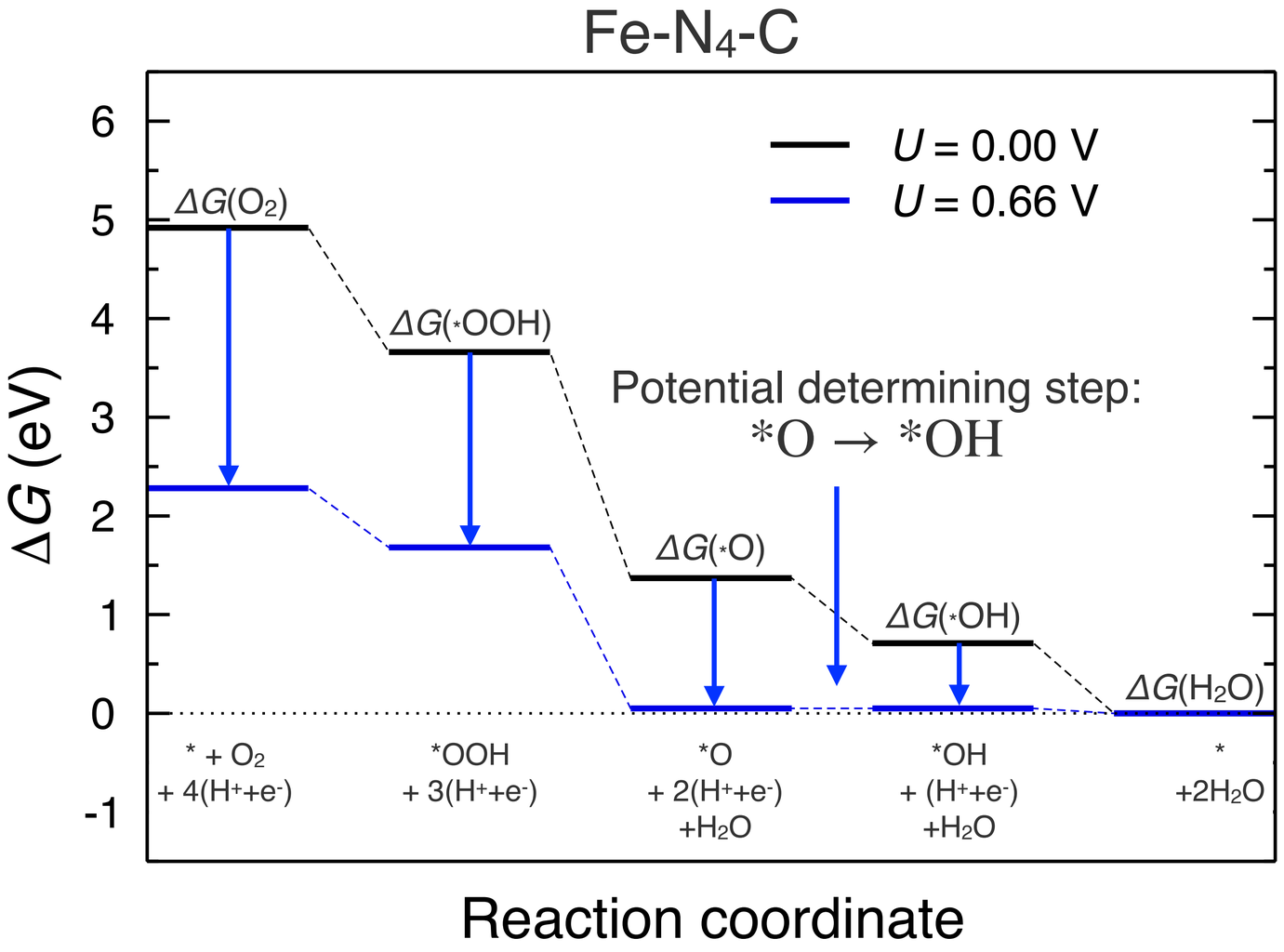

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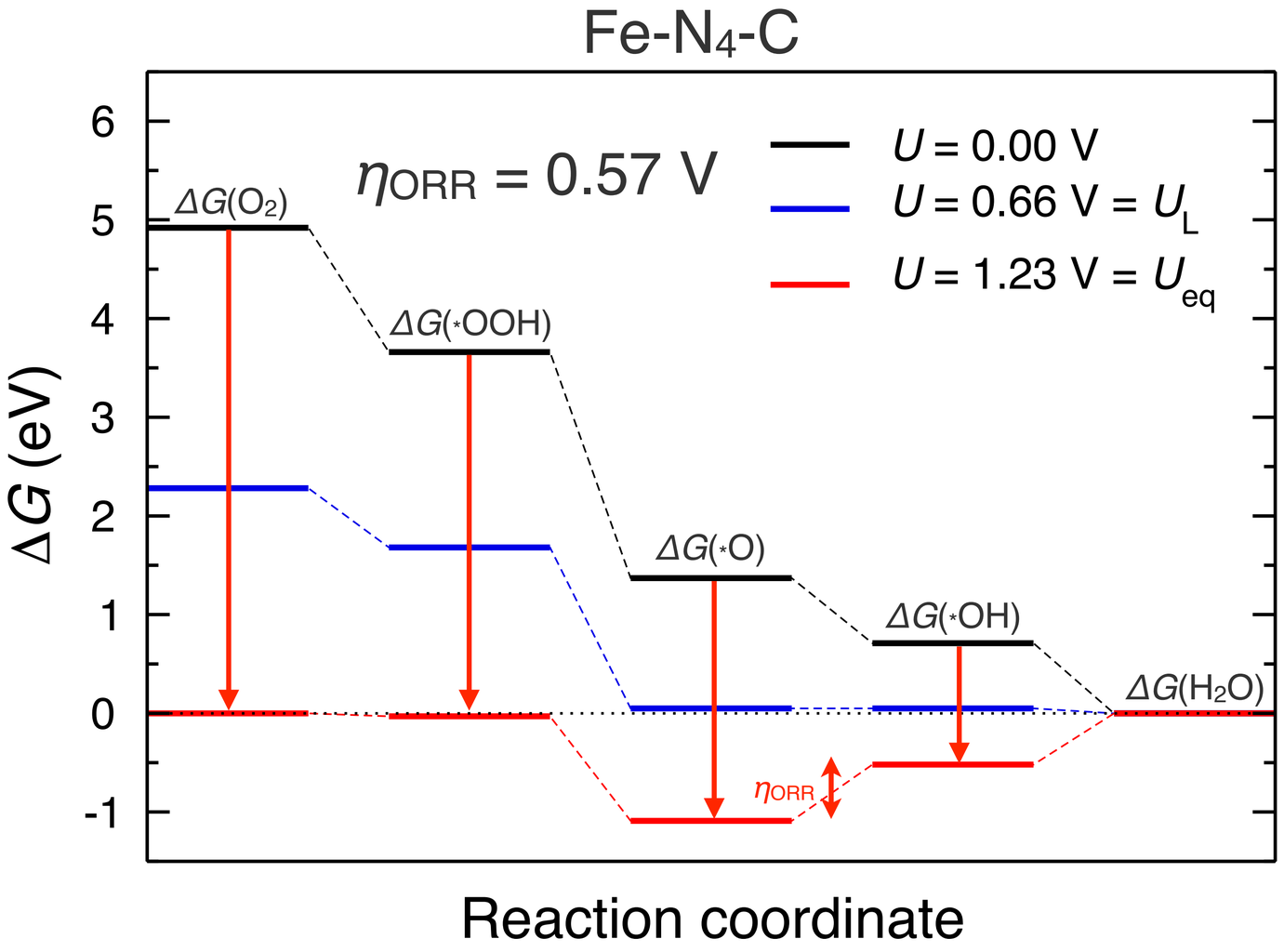

Overpotential: $\eta_{ORR} = U_{eq} - U_L$

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First-principle calculation:
Calculation of the total energy of the many-body system

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Schrödinger equation

$$\hat{H}\,|\,\Psi\rangle = E_{\mathrm{tot}}\,|\,\Psi\rangle$$

First-principle calculation: Calculation of the total energy of the many-body system

Total energy

$$E_{\mathrm{tot}}[\Psi] = \langle \Psi | \hat{H} | \Psi \rangle$$

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Hellman-Feynman theorem

$$\frac{\partial E_{\mathrm{tot}}}{\partial \lambda} = \left\langle \Psi \left| \frac{\partial \hat{H}}{\partial \lambda} \right| \Psi \right\rangle$$

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2*n*+1 theorem

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$$\frac{\partial^2 E_{\text{tot}}}{\partial \lambda_i \partial \lambda_j} = \left\langle \frac{\partial \Psi}{\partial \lambda_j^*} \left| \frac{\partial \hat{H}}{\partial \lambda_i} \right| \Psi \right\rangle + \left\langle \Psi \left| \frac{\partial \hat{H}}{\partial \lambda_i} \right| \frac{\partial \Psi}{\partial \lambda_j} \right\rangle$$

(Many-body) Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 - \sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 + \sum_I \frac{Z_I e^2}{|\mathbf{r} - \mathbf{R}_I|} + \frac{1}{2}\sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{2}\sum_{I \neq J} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|}$$

(Many-body) wave function

$$\Psi = \Psi(\mathbf{r}_1, \mathbf{r}_2, \cdots \mathbf{r}_{N_e}; \mathbf{R}_1, \mathbf{R}_2, \cdots, \mathbf{R}_{N_n})$$

Total energy in density functional theory (DFT)

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Total energy of the electronic system

$$E_{\mathrm{el}}[n] = T_{\mathrm{s}}[n] + \int d\mathbf{r} v_{\mathrm{ext}}(\mathbf{r}) n(\mathbf{r}) + \frac{e^2}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{\mathrm{xc}}[n]$$

Electron density

$$n(\mathbf{r}) = N_e \int \cdots \int d\mathbf{r}_2 \cdots d\mathbf{r}_{N_e} |\Psi(\mathbf{r}, \mathbf{r}_2, \cdots, \mathbf{r}_{N_e})|^2$$

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$$n(\mathbf{r}) = \sum_{m}^{\mathrm{occ}} |\psi_m(\mathbf{r})|^2$$

Hohenberg & Kohn, *Phys. Rev*. **136**, B664 (1964); Kohn & Sham, *Phys. Rev.* **140**, A1133 (1965).

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Exact exchange-correlation (XC) functional *not* known!

Hohenberg & Kohn, *Phys. Rev*. **136**, B664 (1964); Kohn & Sham, *Phys. Rev.* **140**, A1133 (1965).

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$$E_{\mathrm{xc}}^{\mathrm{SL}}[n] = \int d\mathbf{r} f_{\mathrm{xc}}(n(\mathbf{r}), |\nabla n(\mathbf{r})|)$$

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☹ Less accurate for the dispersion interaction

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☹ Less accurate for the dispersion interaction

→ dispersion inclusive methods (DFT-Dx, TS-vdW, XDM, LRD, vdW-DF…)

Dispersion (vdW)-inclusive DFT

Nonempirical XC functional (vdW-DF)

$$E_{\mathrm{xc}} = E_{\mathrm{x}}^{\mathrm{SL}} + E_{\mathrm{c}}^{\mathrm{SL}} + E_{\mathrm{c}}^{\mathrm{nl}}$$

$$E_{\mathrm{c}}^{\mathrm{nl}} = \frac{1}{2}\iint d\mathbf{r}_1 d\mathbf{r}_2 n(\mathbf{r}_1)\phi(q_1|r_1 - r_2|, q_2|r_1 - r_2|)n(\mathbf{r}_2)$$

Semiempirical XC functional (e.g., DFT-D3)

$$E_{\mathrm{xc}} = E_{\mathrm{x}}^{\mathrm{SL}} + E_{\mathrm{c}}^{\mathrm{SL}} + E_{\mathrm{disp}}$$

$$E_{\mathrm{disp}} = E^{(2)} + E^{(3)}$$

$$E^{(2)} = -\frac{1}{2}\sum_{A\neq B}\sum_{(n=6,8,\cdots)} s_n f_{d,n}(R_{AB})\frac{C_n^{AB}}{R_{AB}^n}$$

$$E^{(3)} = -\frac{1}{6}\sum_{A\neq B} f_{d,9}(\bar{R}_{ABC})\frac{C_9^{ABC}(3\cos\theta_a\cos\theta_b\cos\theta_c + 1)}{(R_{AB}R_{BC}R_{CA})^3}$$

Berland *et al.*, *Rep. Prog. Phys.* **78**, 066501 (2015); Grimme, *et al.*, *Chem. Rev.* **116**, 5105 (2016).

Dispersion (vdW)-inclusive DFT

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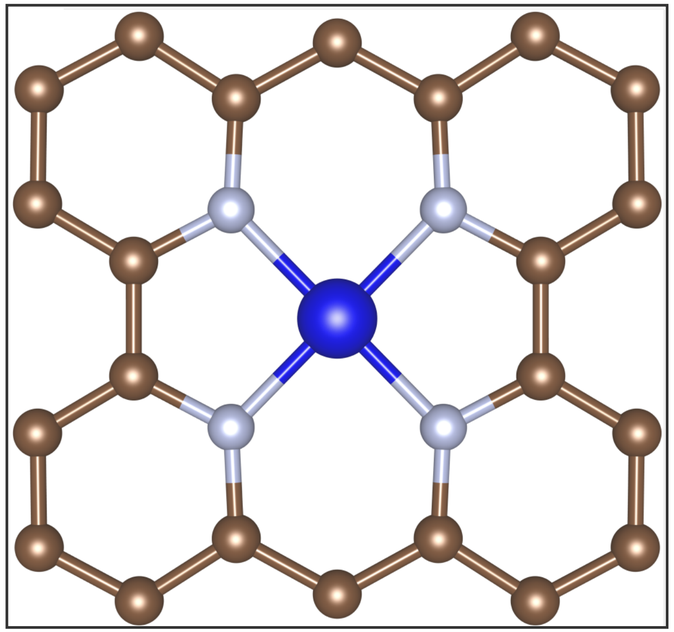
☹ **Accuracy depends on the exchange-correlation functional used**

Berland *et al.*, *Rep. Prog. Phys.* **78**, 066501 (2015); Grimme, *et al.*, *Chem. Rev.* **116**, 5105 (2016).

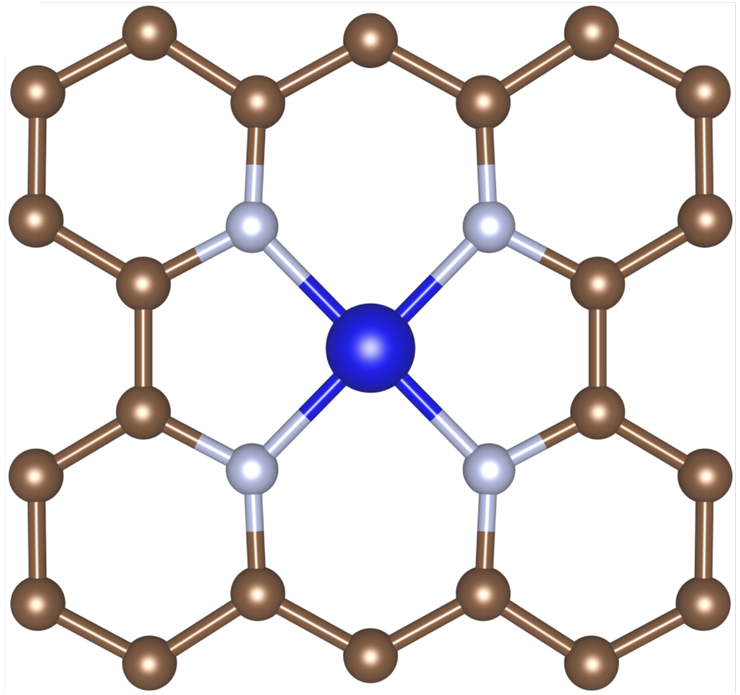
Computational details

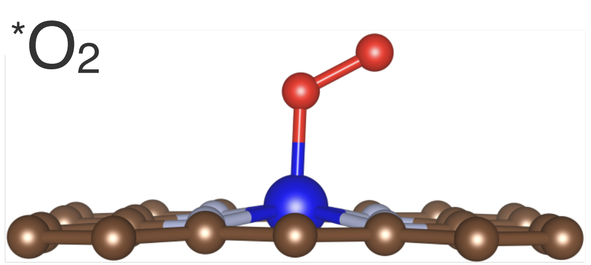
- Quantum-ESPRESSO
  - Projector augmented wave potentials
  - Plane-wave basis
  - PBE, PBE-D3, RPBE, RPBE-D3
    (D3: Grimme's dispersion correction)
  - Bayesian error estimate functional (BEEF-vdW)
    as a reference
- Fe-N_4-C & Co-N_4-C models
  - Graphene (5×5) supercell
  - Vacuum condition
  - CHE to estimate the limiting- and over-potentials of ORR

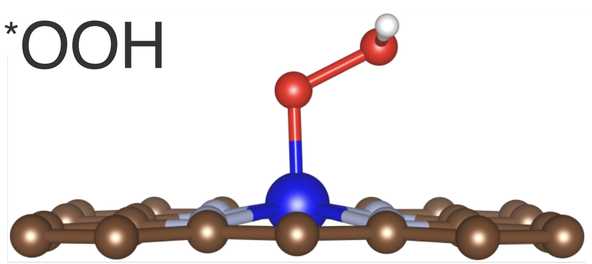


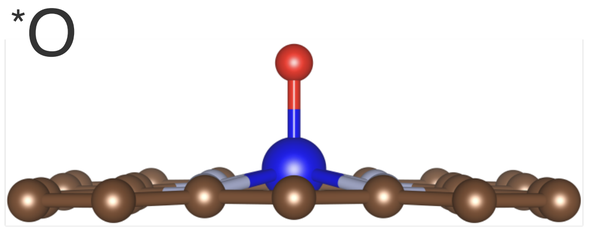
BEEF-vdW: Wellendorff *et al.*, *Phys. Rev. B* **85**, 235149 (2012).

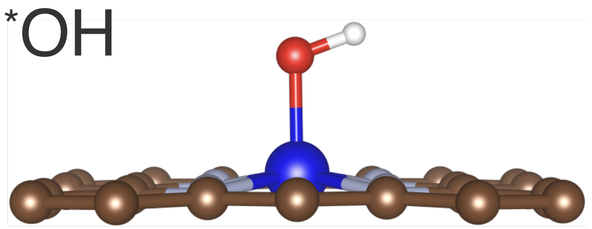
ORR intermediates on Fe-N_4-C and Co-N_4-C



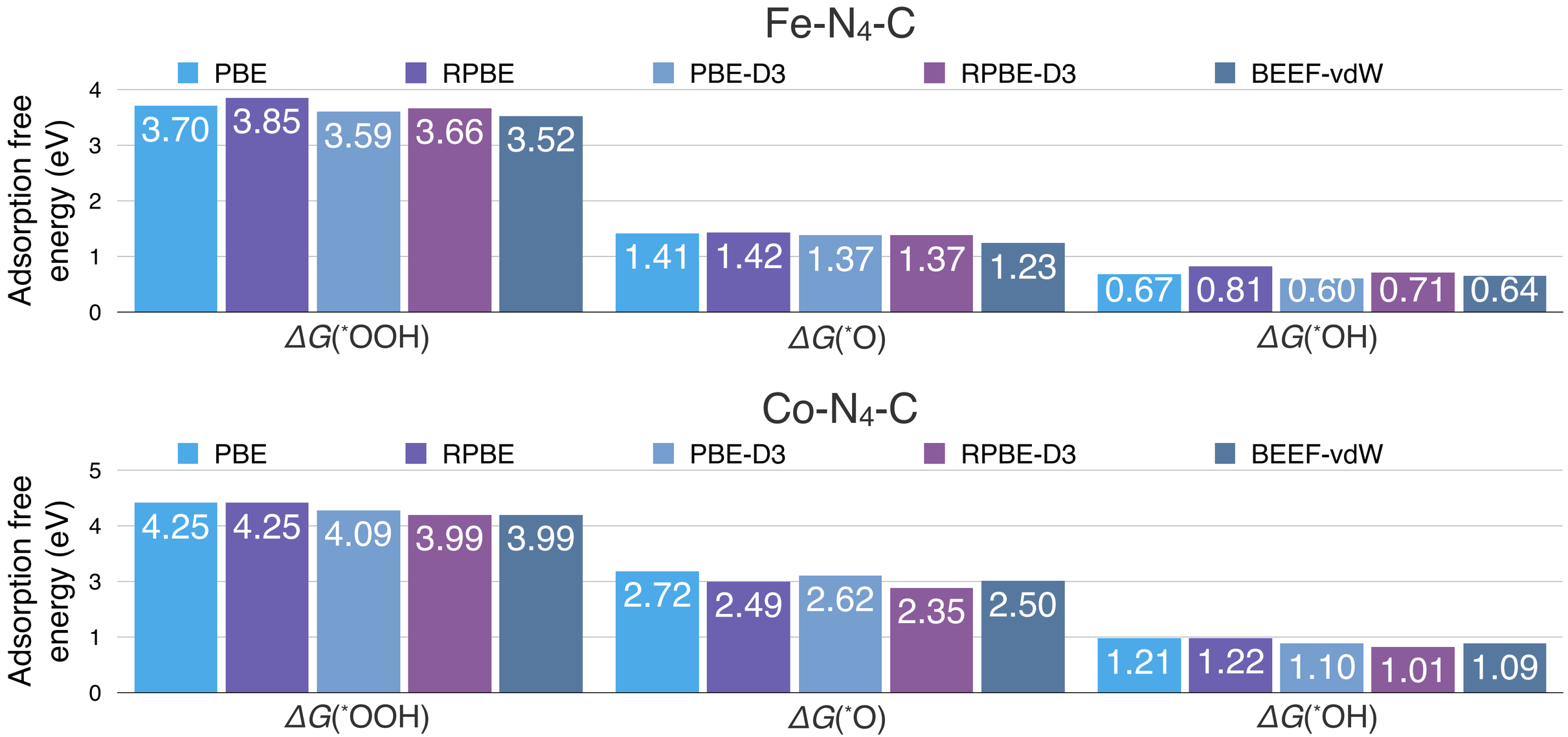




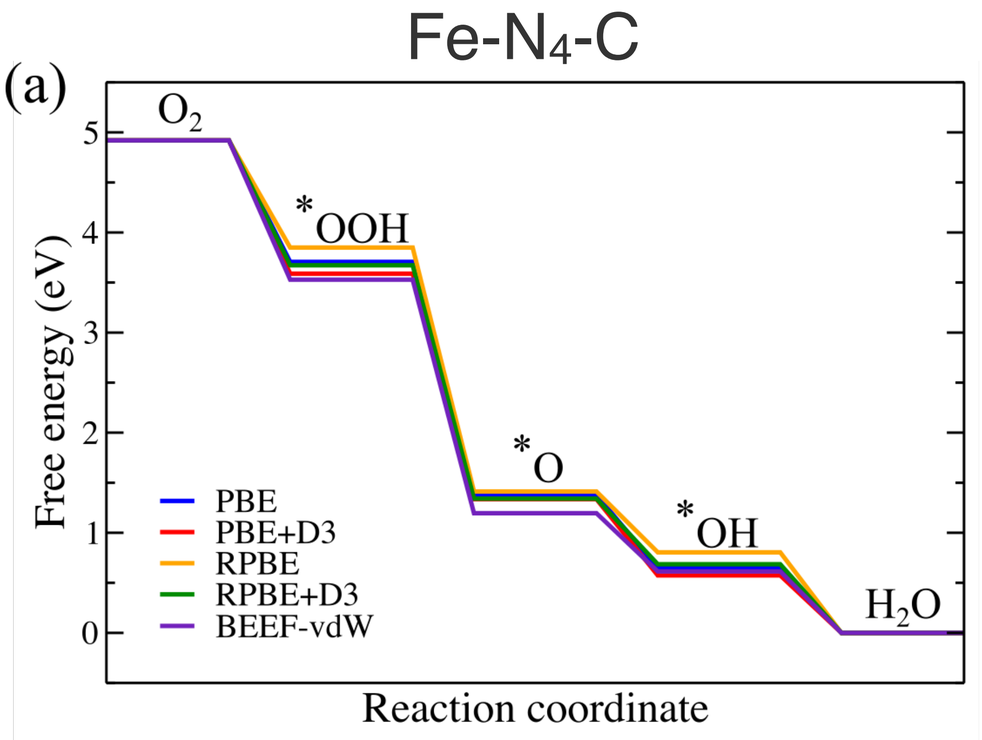


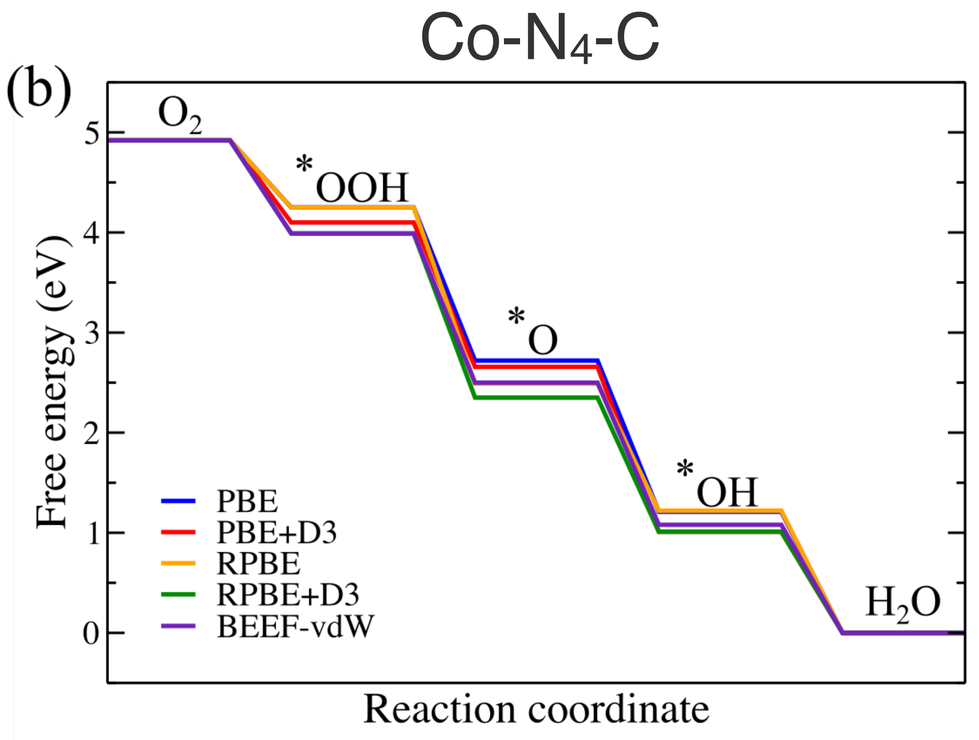


Adsorption free energy (U = 0 V)

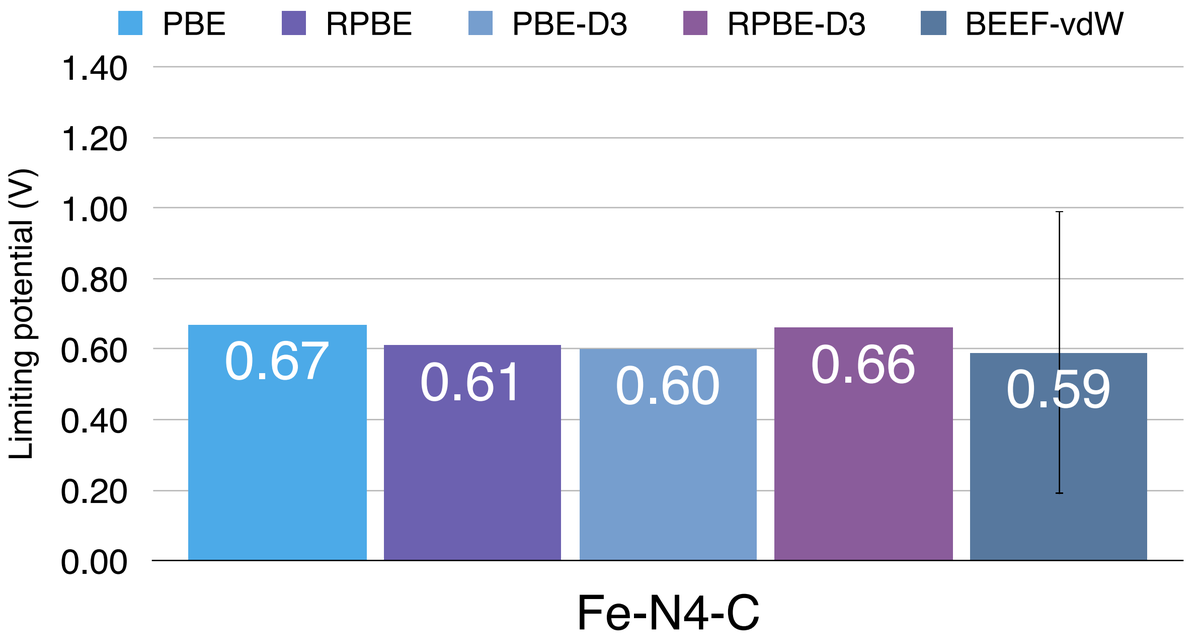


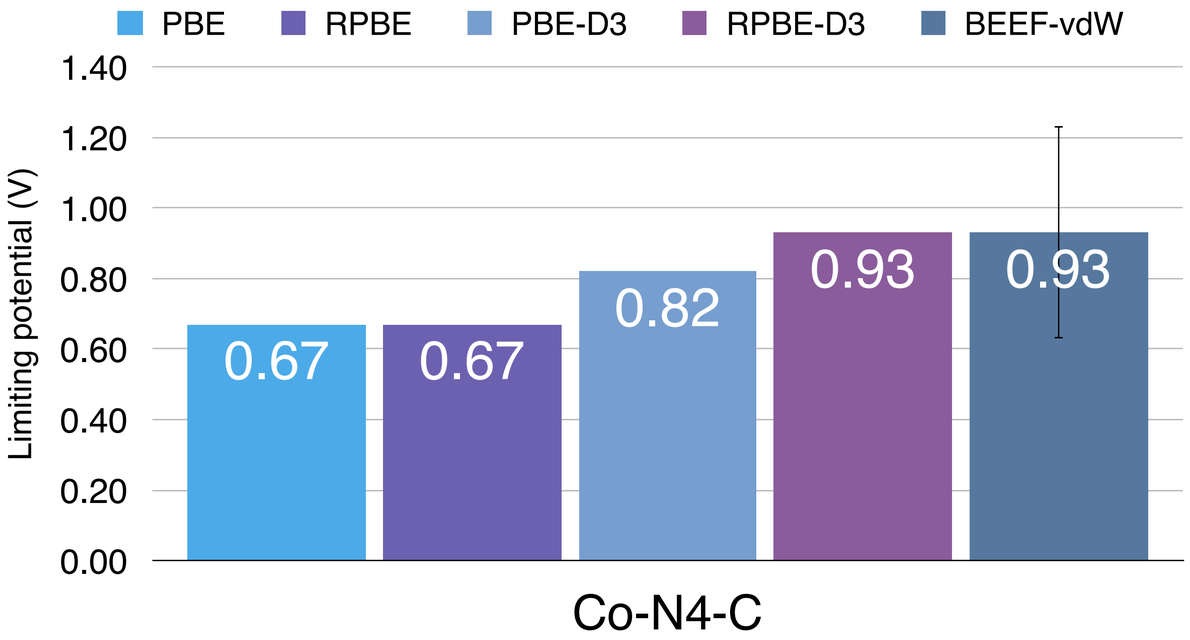
Free energy diagram (U = 0 V)





Catalyst activity — limiting potential





Potential determining step (PDS)

	PBE	RPBE	PBE-D3	RPBE-D3	BEEF-vdW
Fe-N_4-C	*OH→H_2O	*O→*OH	*OH→H_2O	*O→*OH	*O→*OH
Co-N_4-C	*O→*OH	*O→*OH	*O→*OH	*O→*OH	*O→*OH

RPBE-D3 is the most consistent with BEEF-vdW

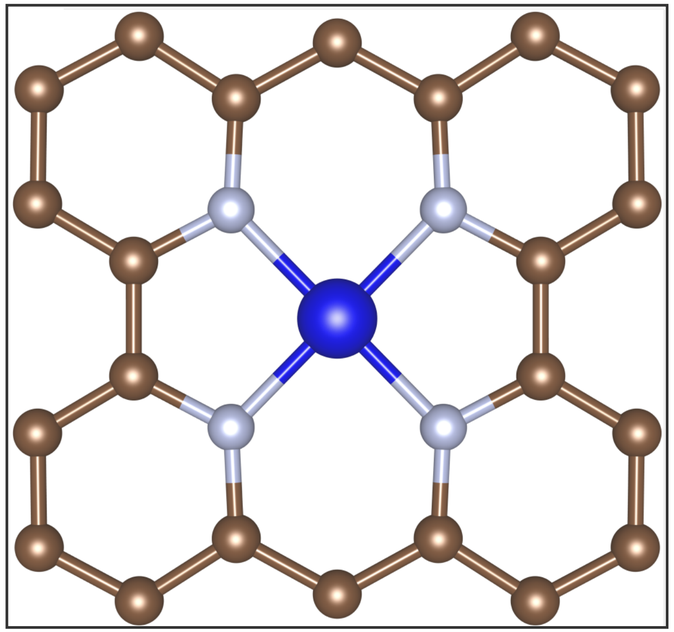
Abidin and IH, *Surf. Sci.* **724**, 122144 (2022).

Outline

- Introduction
  - Transition metal (Fe, Co) single atom catalysts for the oxygen reduction reaction (ORR)
- Computational hydrogen electrode model
- Exchange-correlation functional dependence of the ORR activity
- ORR activity of Fe-N_4-C and Co-N_4-C from ESM-RISM
  - Solvent effect
  - Electrode-potential effect
- Summary

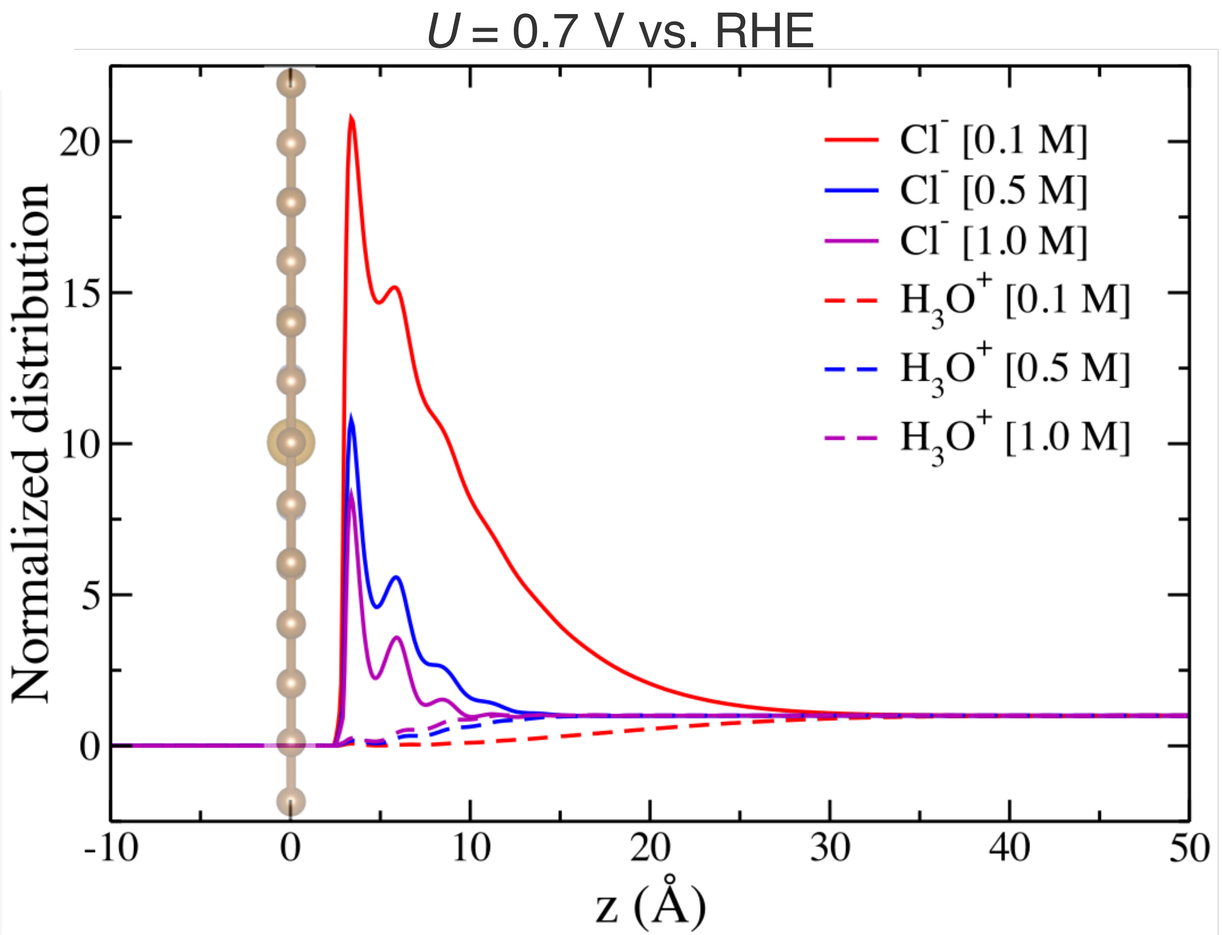
Computational details

- Quantum-ESPRESSO
  - Projector augmented wave potentials
  - Plane-wave basis
  - RPBE-D3
  - ESM-RISM
    - SPC & TIP5P for H_2O
    - L-J potentials for H_3O^+ and other atoms/ions
- Fe-N_4-C & Co-N_4-C models
  - Graphene (5×5) supercell
  - HCl solution to model an acidic environment (H_3O^+ & Cl^-, 0, 0.1, 0.5, 1.0 M)



FF parameters: Haruyama *et al.*, *Phys. Rev. Materials*. **2**, 095801 (2018).
C & N FF parameters: Abidin and IH, *Phys. Rev. B* **105**, 075416 (2022).

Distribution of electrolyte ions in a HCl solution



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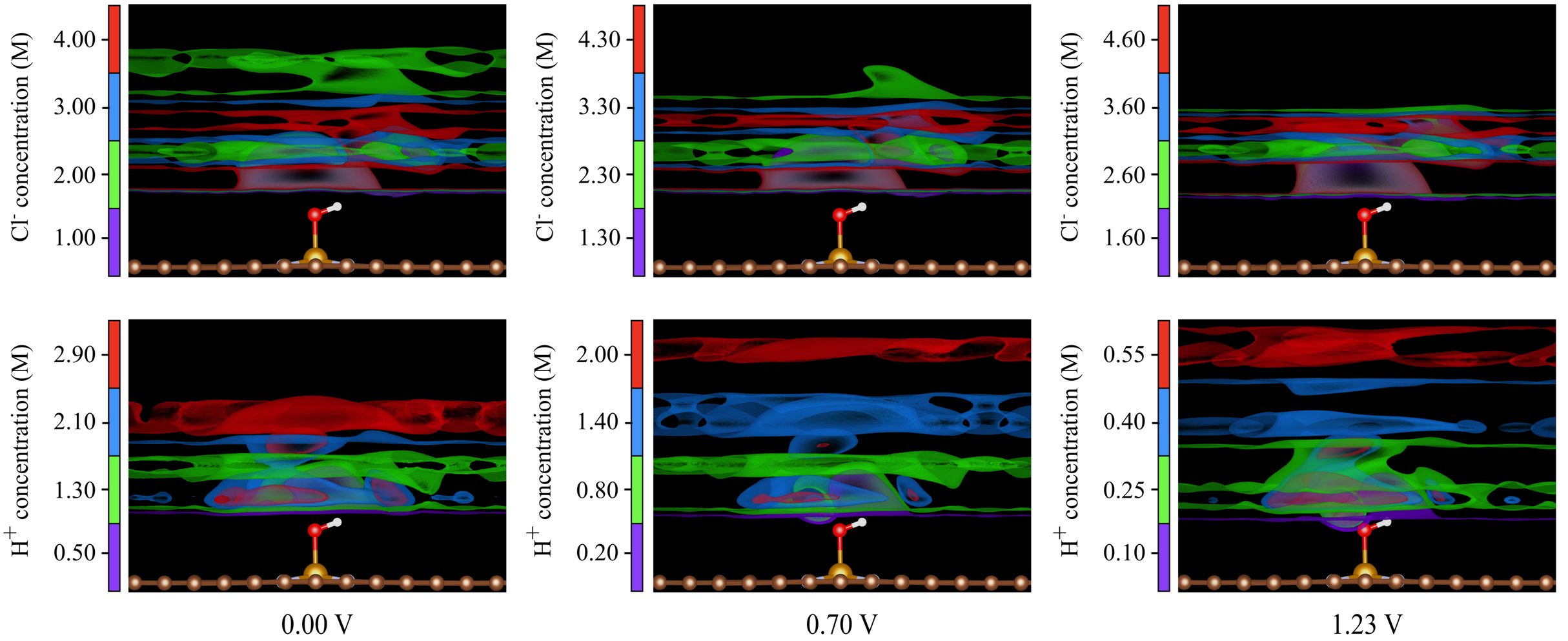


ORR mechanism on TM-N_4-C

ORR mechanism on TM-N_4-C

4-electron associative mechanism (in an acid electrolyte)

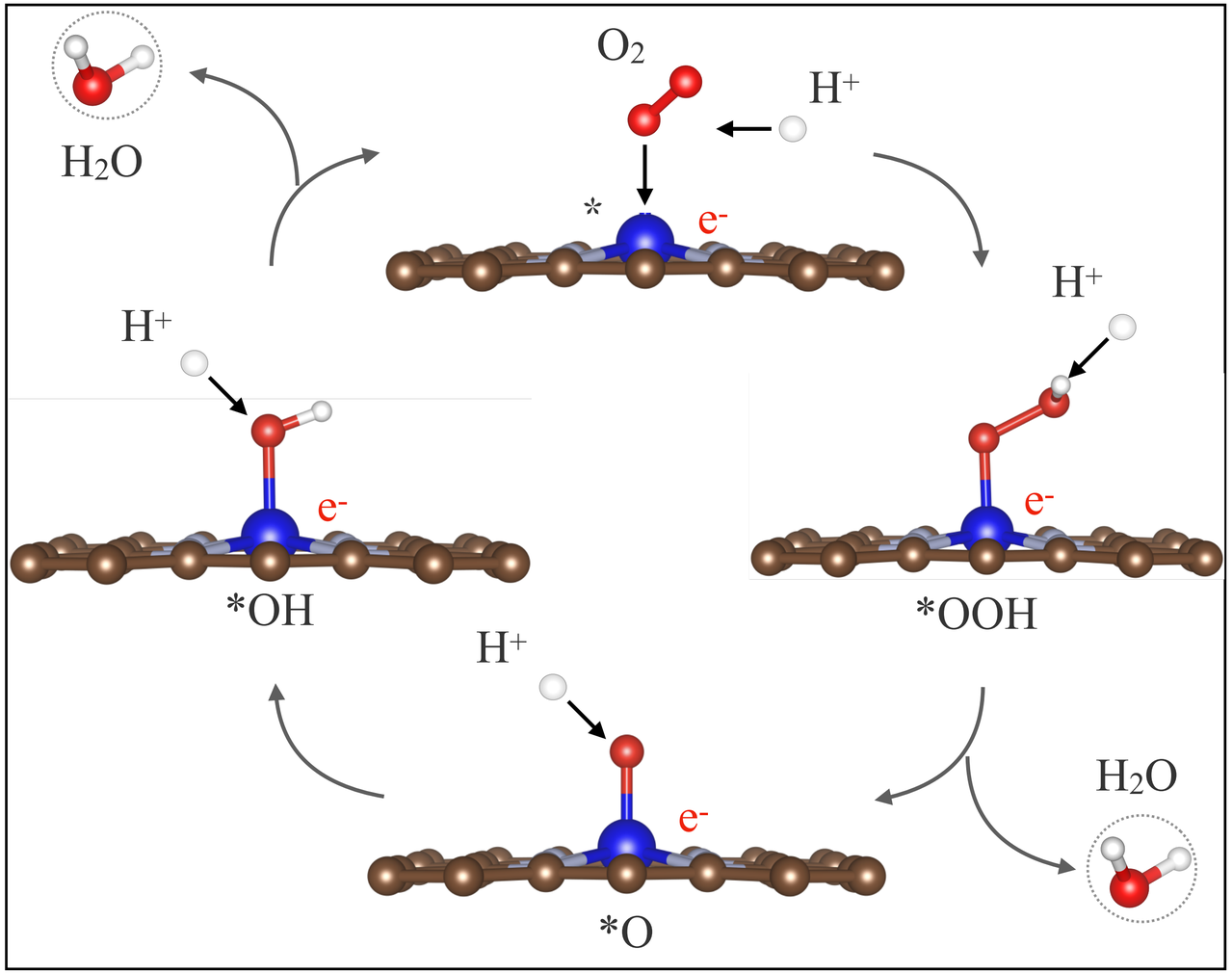
$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

$$O_2 + H^+ + e^- + * \rightarrow * OOH$$

$$*OOH + H^+ + e^- \rightarrow *O + H_2O$$

$$*O + H^+ + e^- \rightarrow *OH$$

$$*OH + H^+ + e^- \rightarrow H_2O$$



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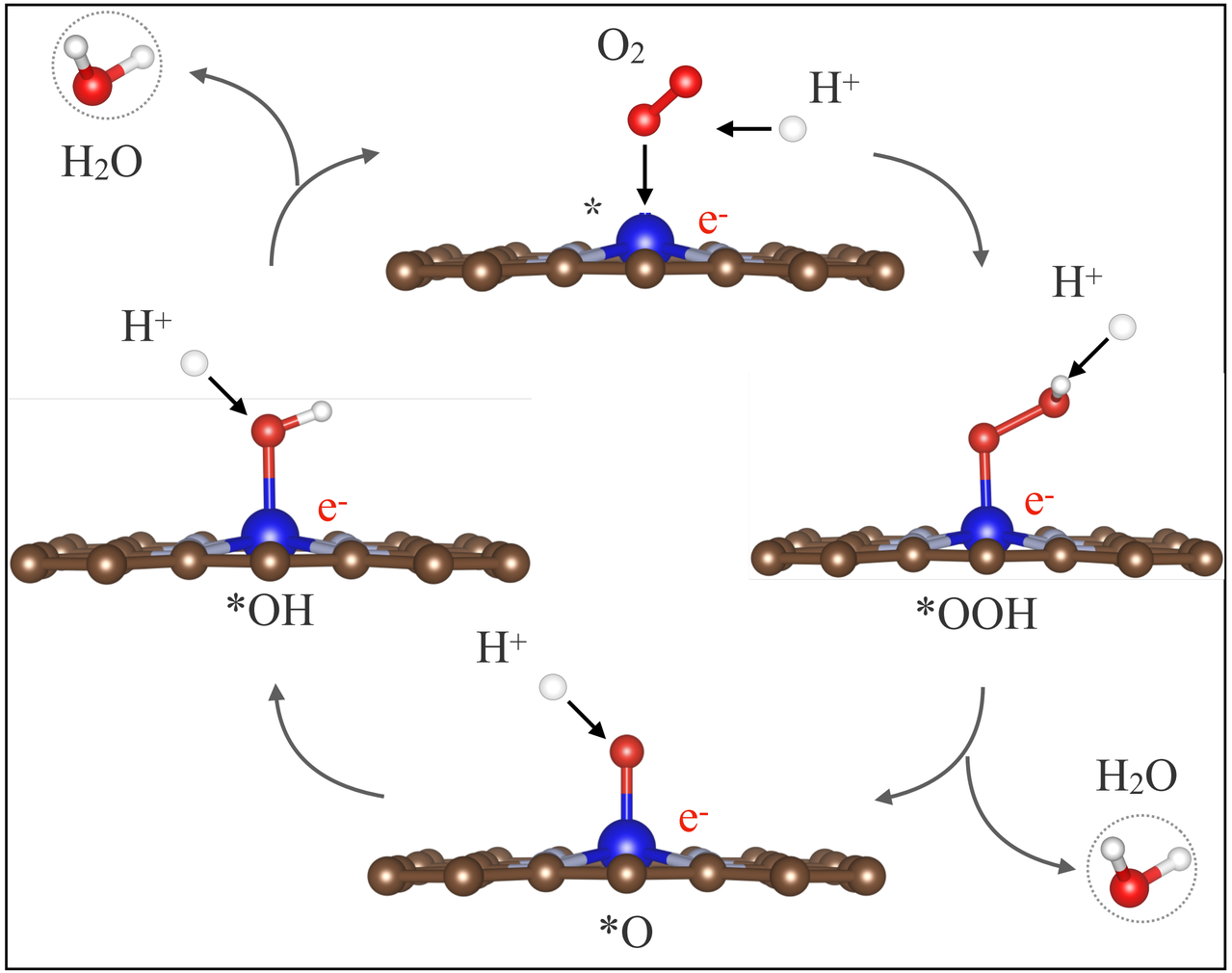
$$*OOH + H^+ + e^- \rightarrow *O + H_2O \quad \Delta G(*O)$$

$$*O + H^+ + e^- \rightarrow *OH \quad \Delta G(*OH)$$

$$*OH + H^+ + e^- \rightarrow H_2O \quad \Delta G(H_2O)$$



Free energies of ORR intermediates

Constant-*N* (neutral) / CHE method

$$G = A + E_{\mathrm{ZPE}} - TS$$

$$A = E_{\mathrm{tot}} + \Delta A_{\mathrm{solv}}$$

Constant-electrode potential (constant-μ) methods

$$G = \Omega + E_{\mathrm{ZPE}} - TS$$

$$\Omega = E_{\mathrm{tot}} + \Delta A_{\mathrm{solv}} - \Delta N_{\mathrm{e}} \mu_{\mathrm{e}}$$

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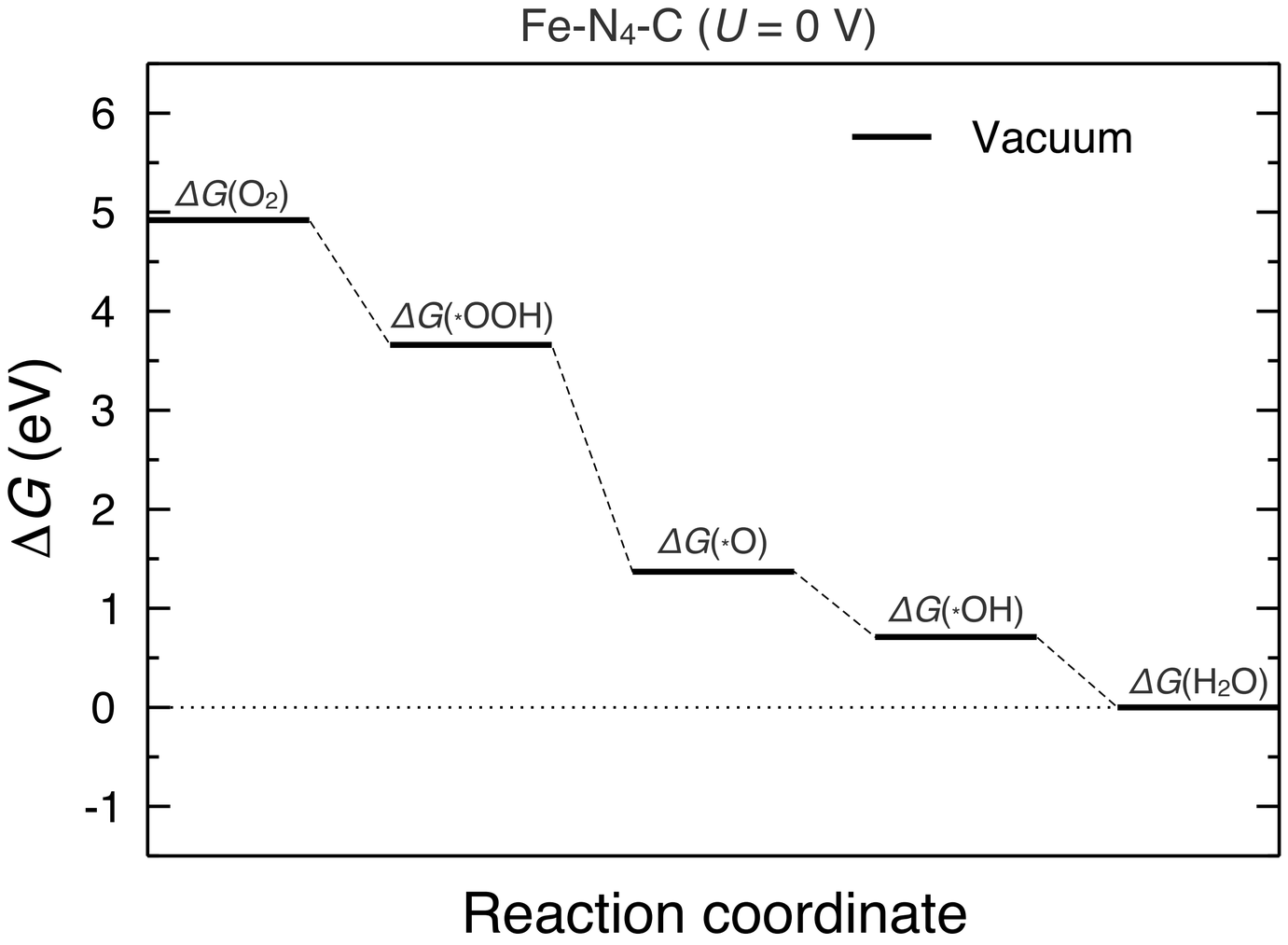
Effect of the electrode potential is included in μ_{e}
(no additional potential U needed)

Effect of the solvent (constant-*N* / CHE)



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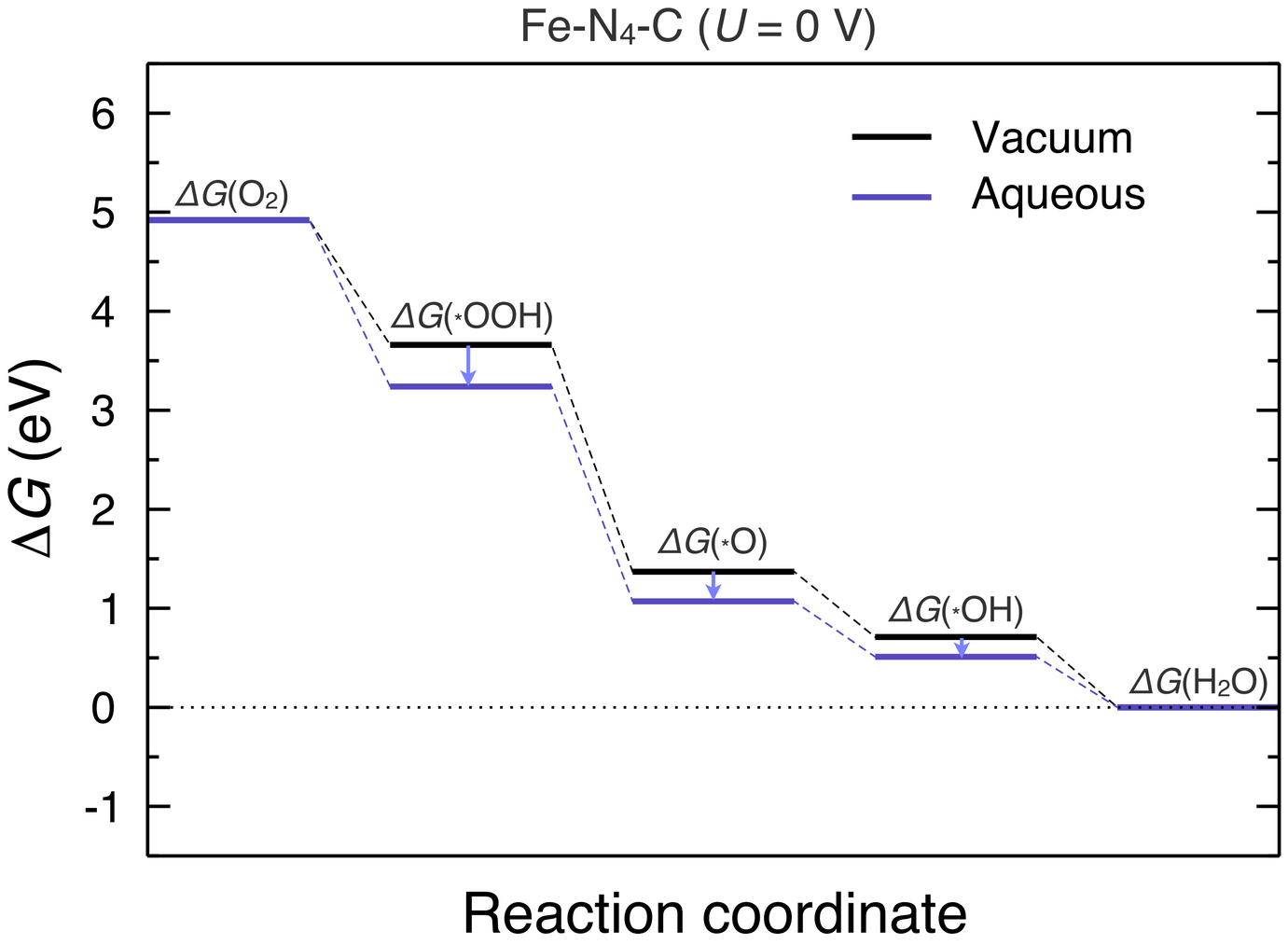
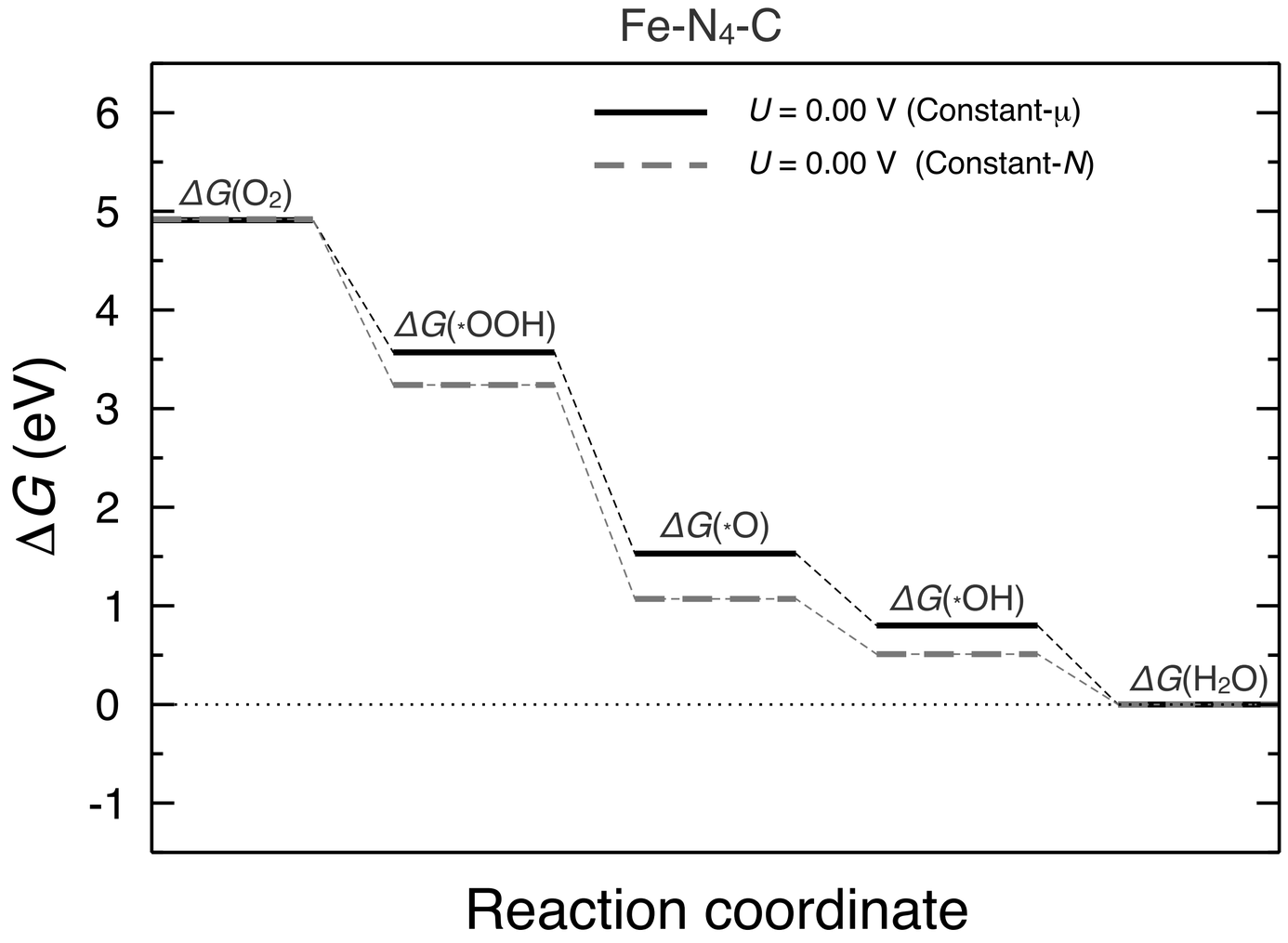


Solvent (water) stabilizes the ORR intermediates

Effect of the electrode potential with ESM-RISM



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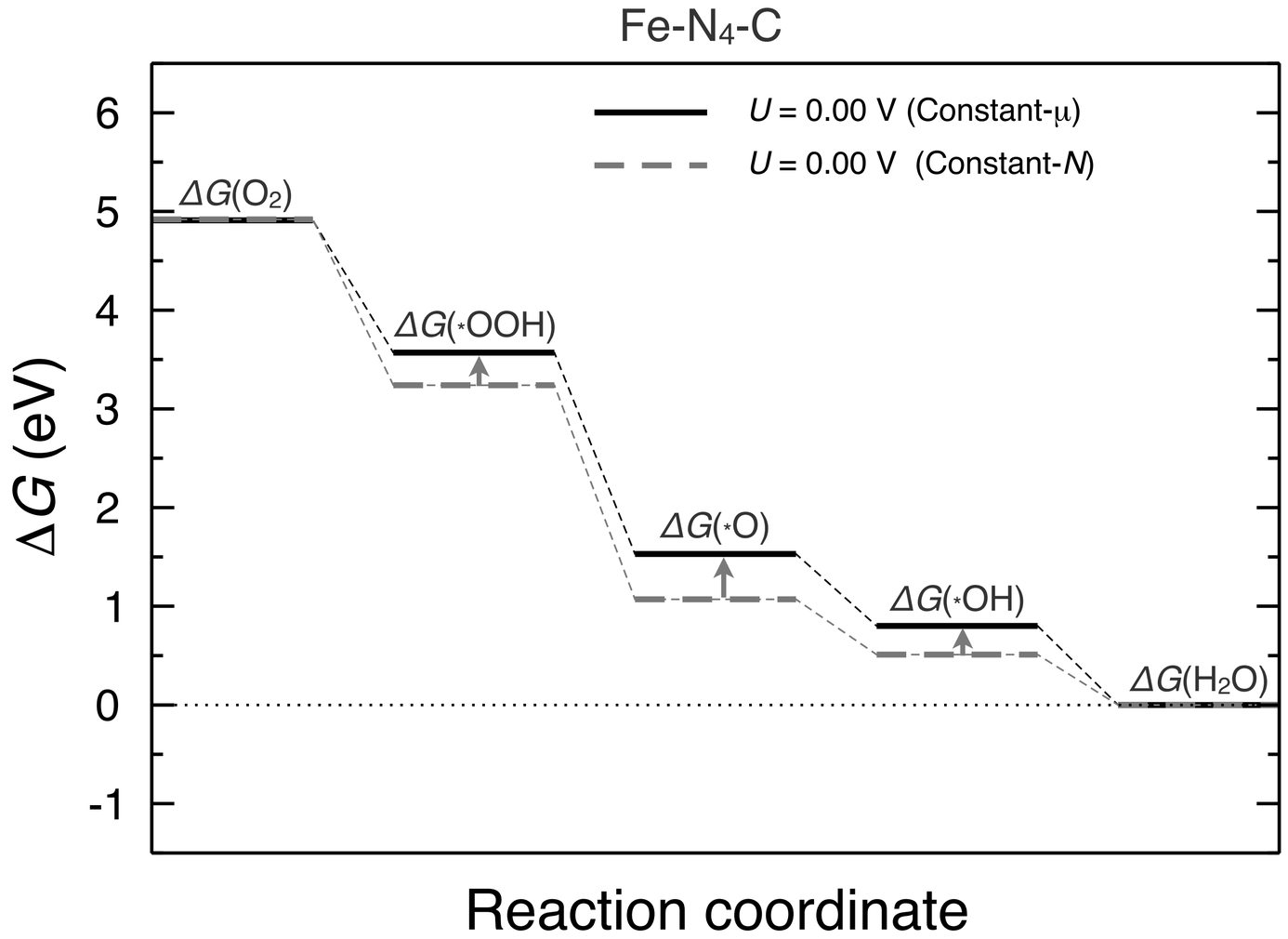
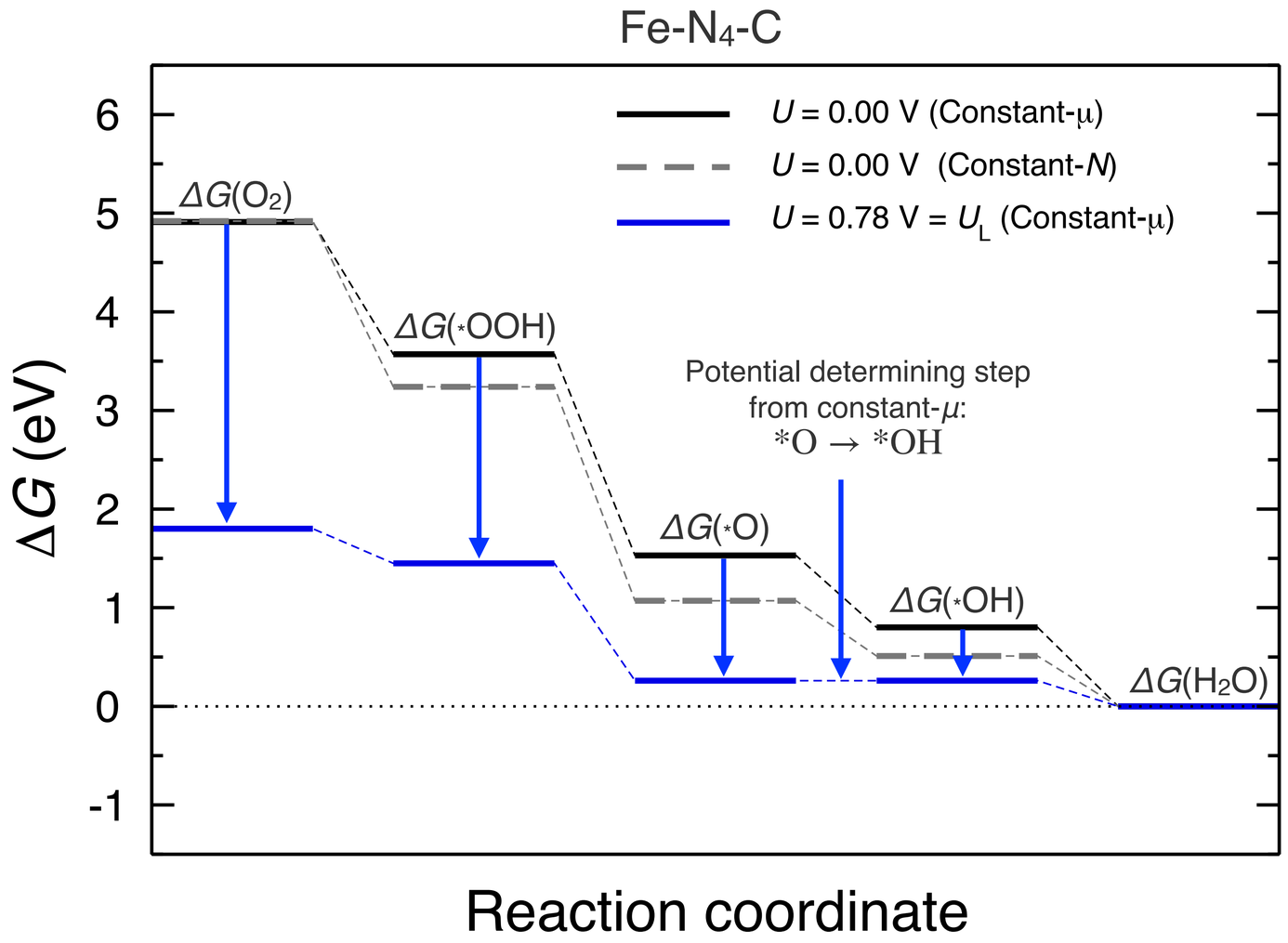


Increase in the adsorption free energy from constant-*N* (neutral) to constant-μ

Effect of the electrode potential with ESM-RISM



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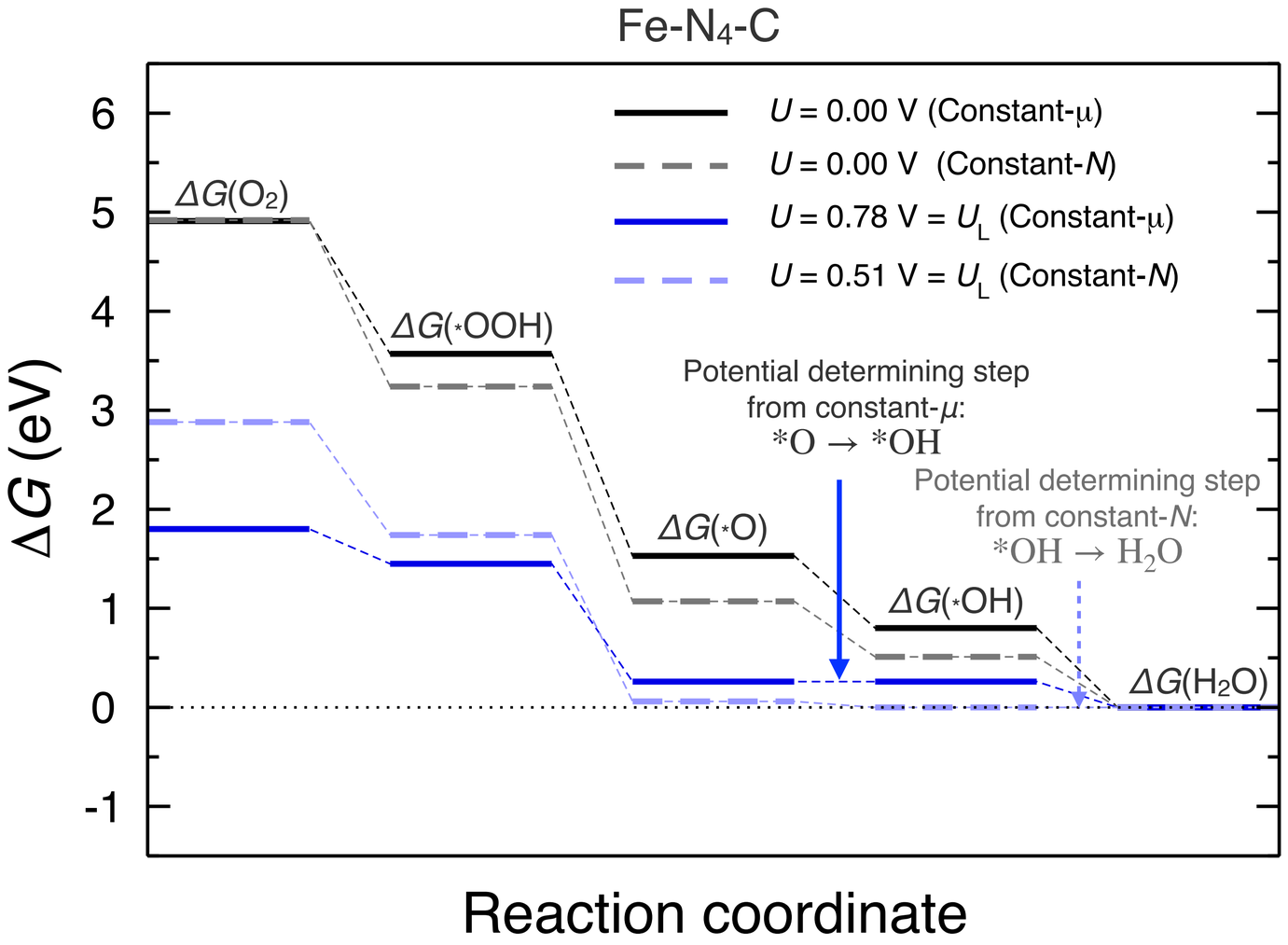
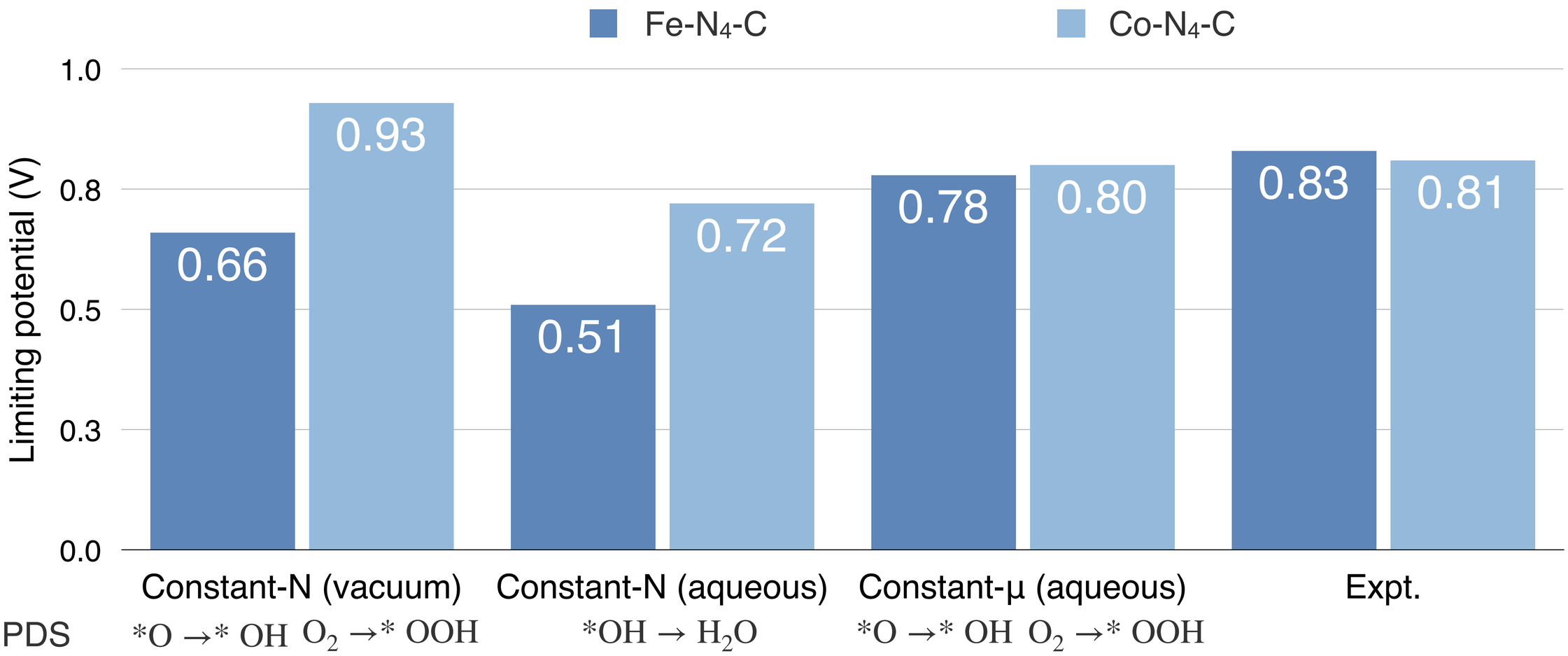


Increase in the adsorption free energy from constant-*N* (neutral) to constant-μ

Change in the limiting step (and potential) from constant-*N* (neutral) to constant-μ

Summary — Limiting potentials of Fe-N_4-C and Co-N_4-C



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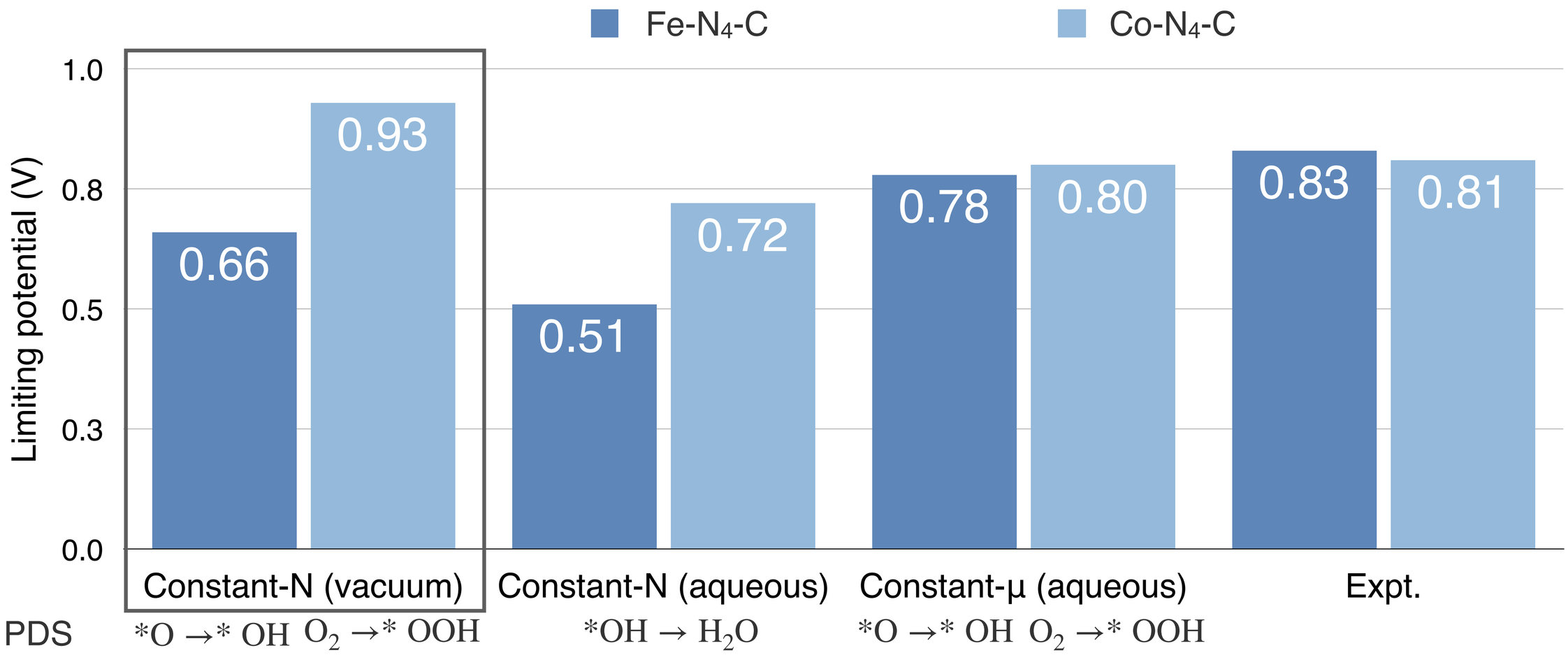

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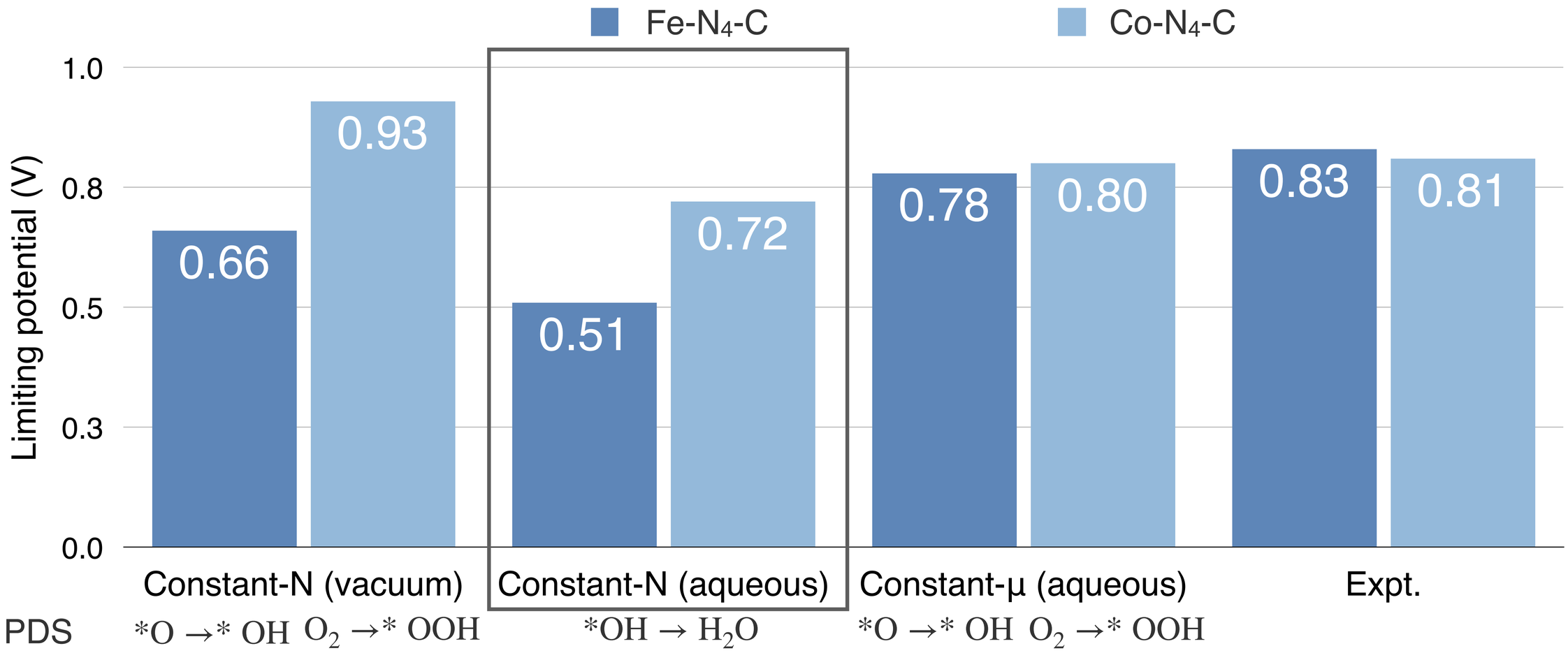

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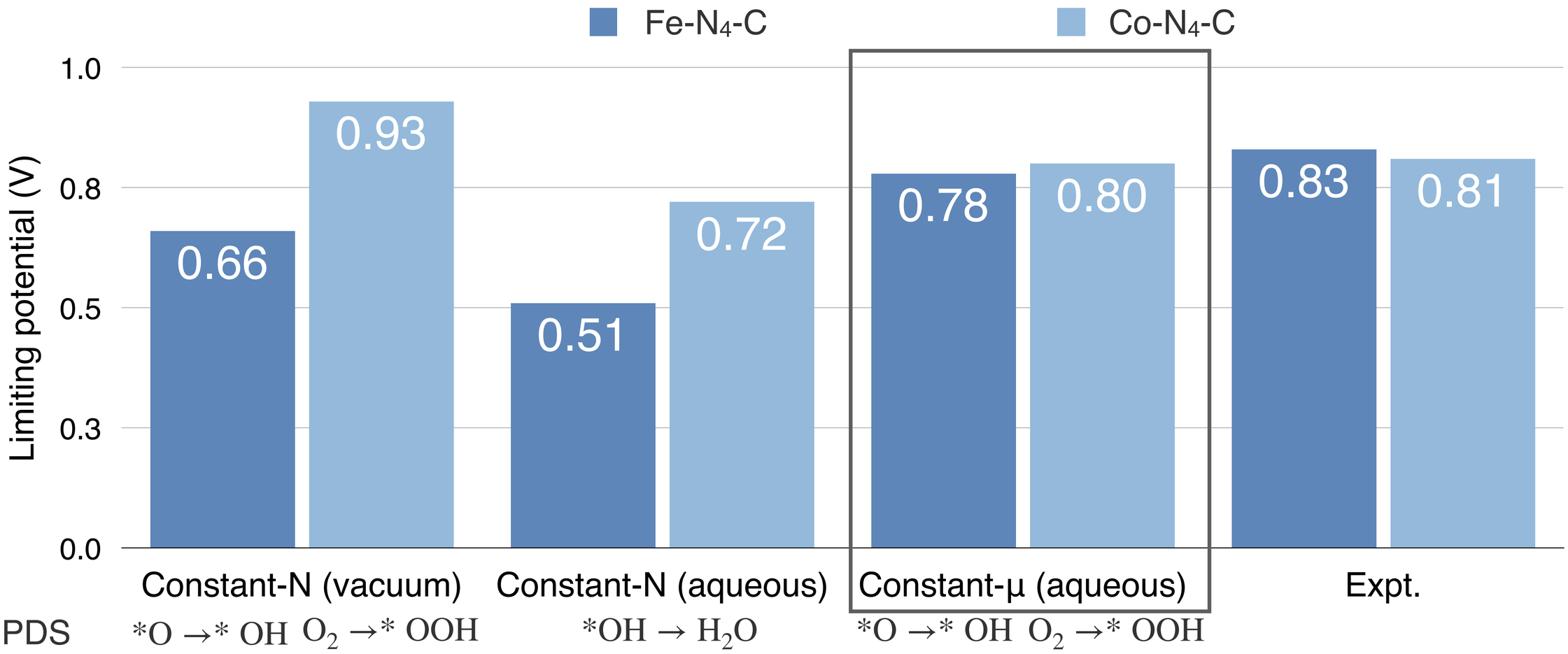

☻ Constant-μ method seems to improve the agreement with the experiments

Possible origin of the differences: surface charge

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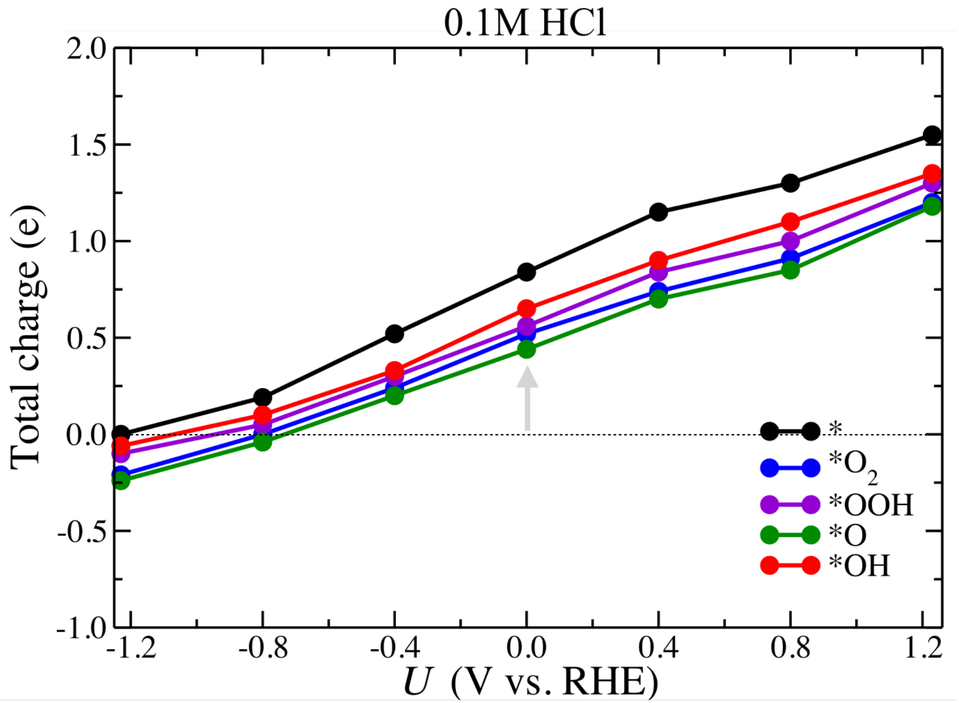
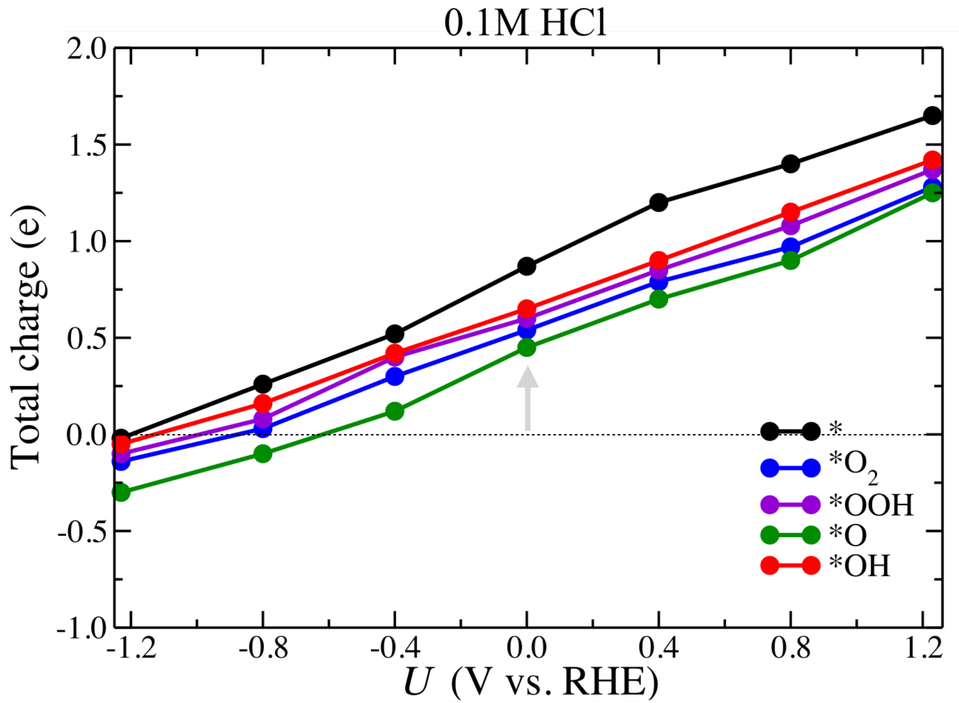
Total charges from constant-μ (constant potential) calculations

Fe-N_4-C



Co-N_4-C

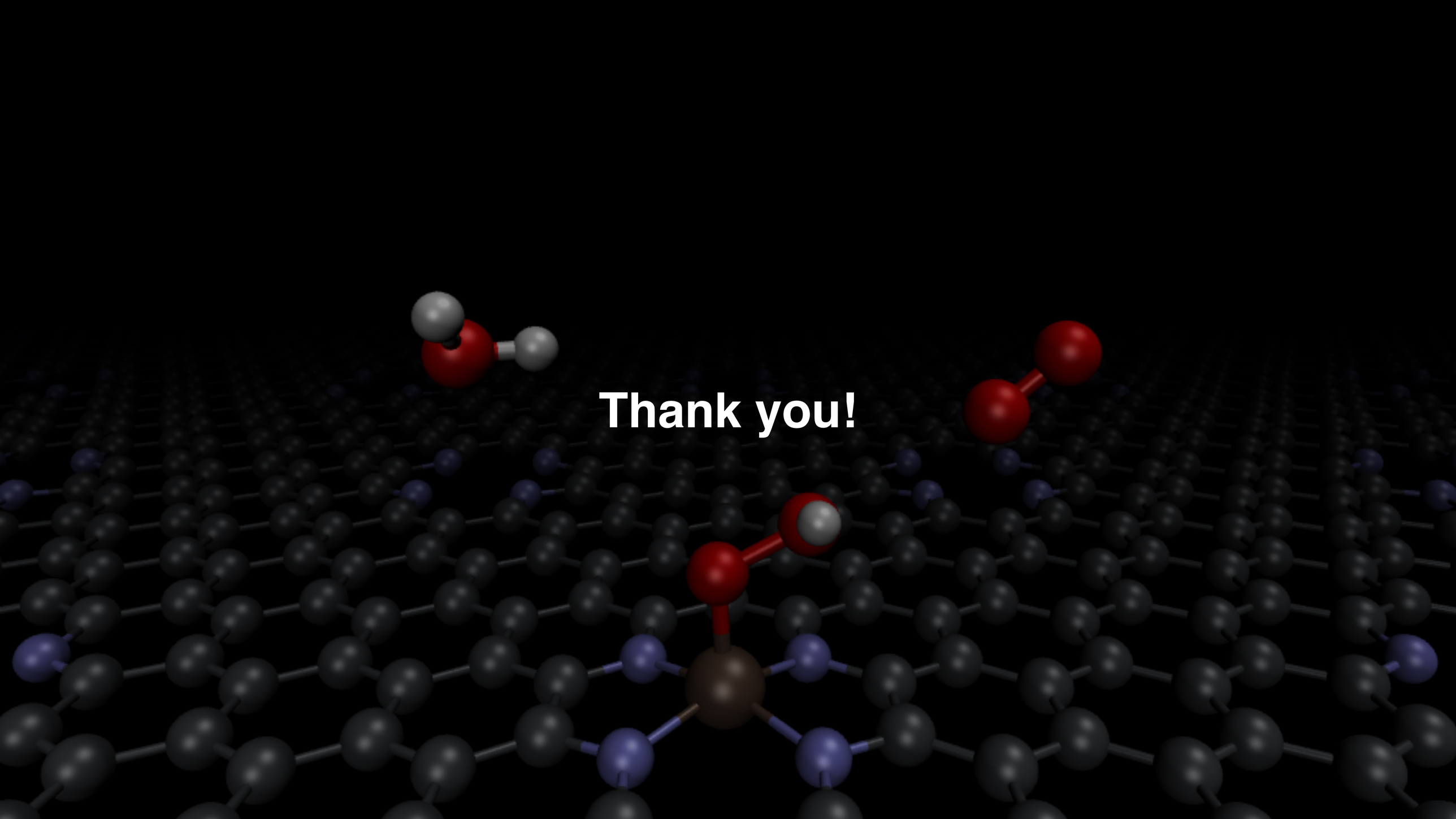


Systems are not neutral, even at $U_{RHE} = 0$

Summary

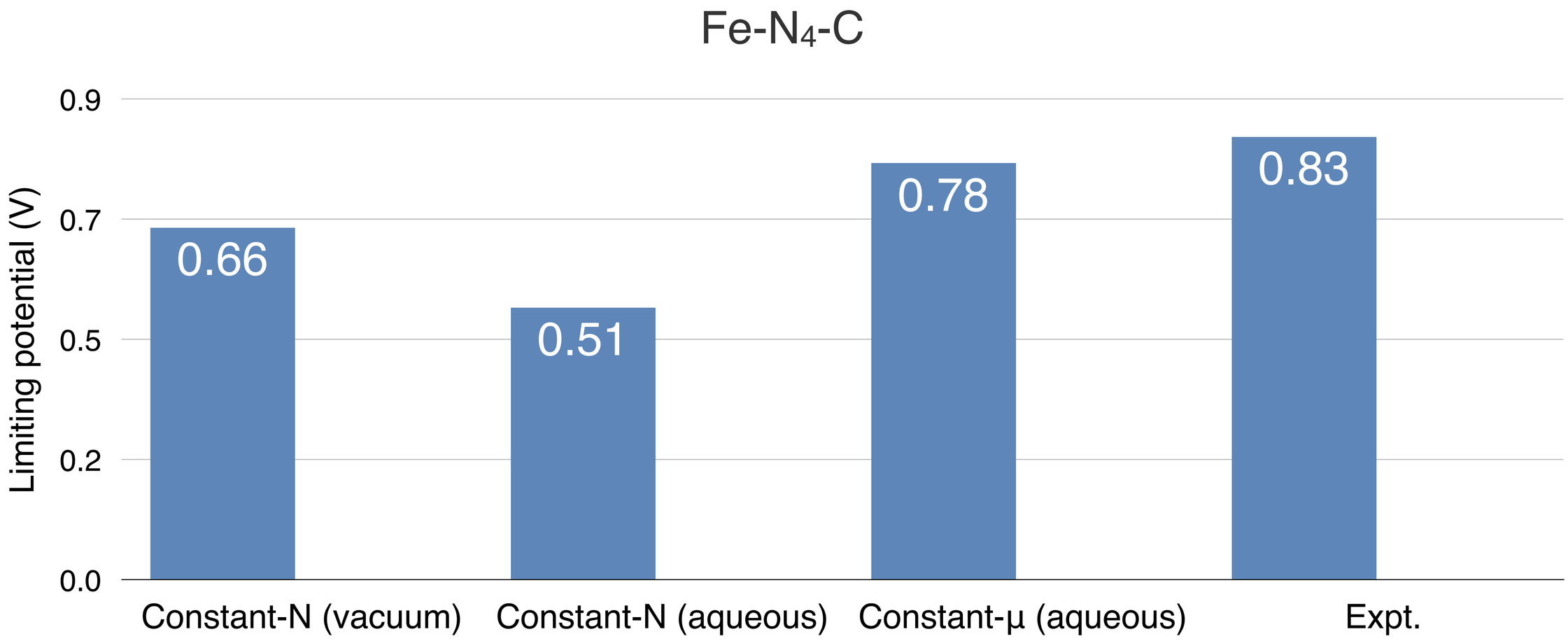
- Systematic DFT study of electrochemical ORR on Fe-N_4-C and Co-N_4-C with ESM-RISM
  - Choice of the exchange-correlation functional
  - Effect of the solvent
  - Effect of the electrode potential via the constant-potential calculations
- The results obtained using both constant-potential and ESM-RISM (more) consistent with the experiments

Abidin and IH, *Phys. Rev. B* **105**, 075416 (2022).
Abidin and IH, *Surf. Sci*. **724**, 122144 (2022).
Abidin and IH, *J. Phys. Chem*. *C* **127**, 13623 (2023).


Thank you!

Backups

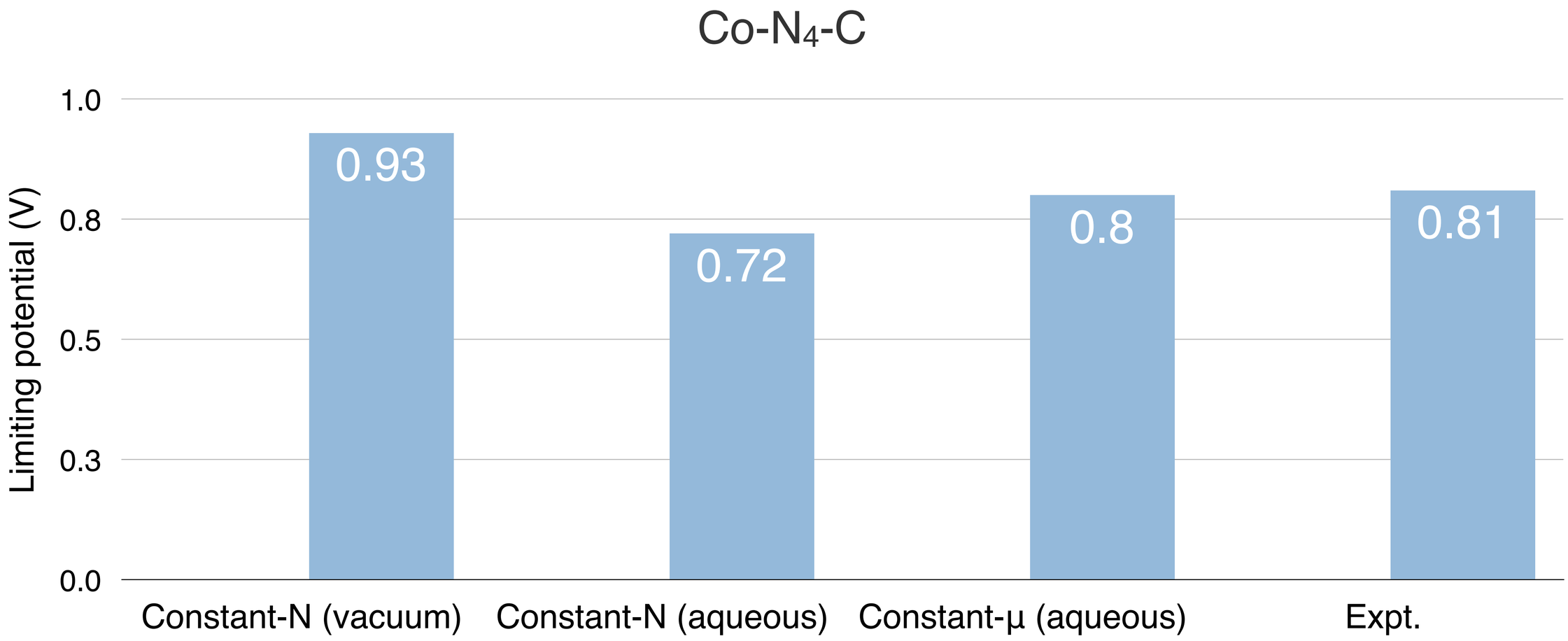
Summary — Limiting potential



PDS (potential determining step)

Constant-N (vacuum)	Constant-N (aqueous)	Constant-μ (aqueous)
*O → * OH	*OH → H_2O	*O → * OH

Summary — Limiting potential

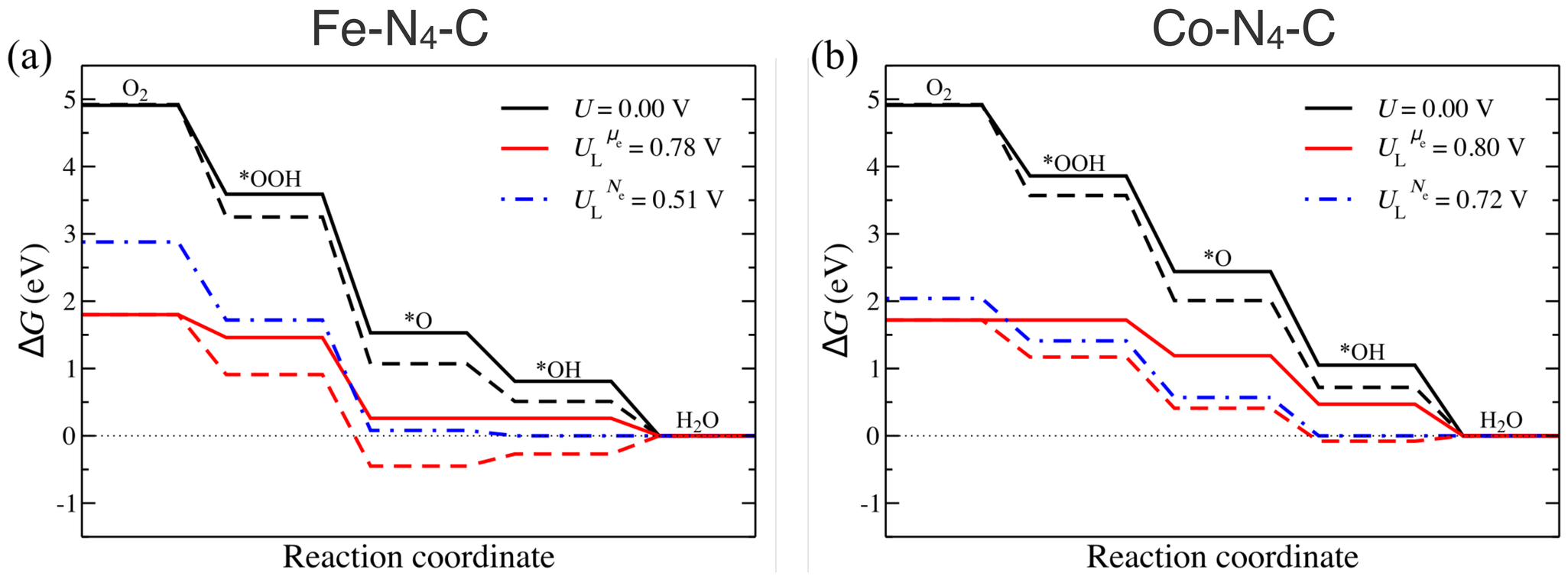


PDS (potential determining step)

$O_2 \rightarrow * OOH$ $\quad$ $*OH \rightarrow H_2O$ $\quad$ $O_2 \rightarrow * OOH$

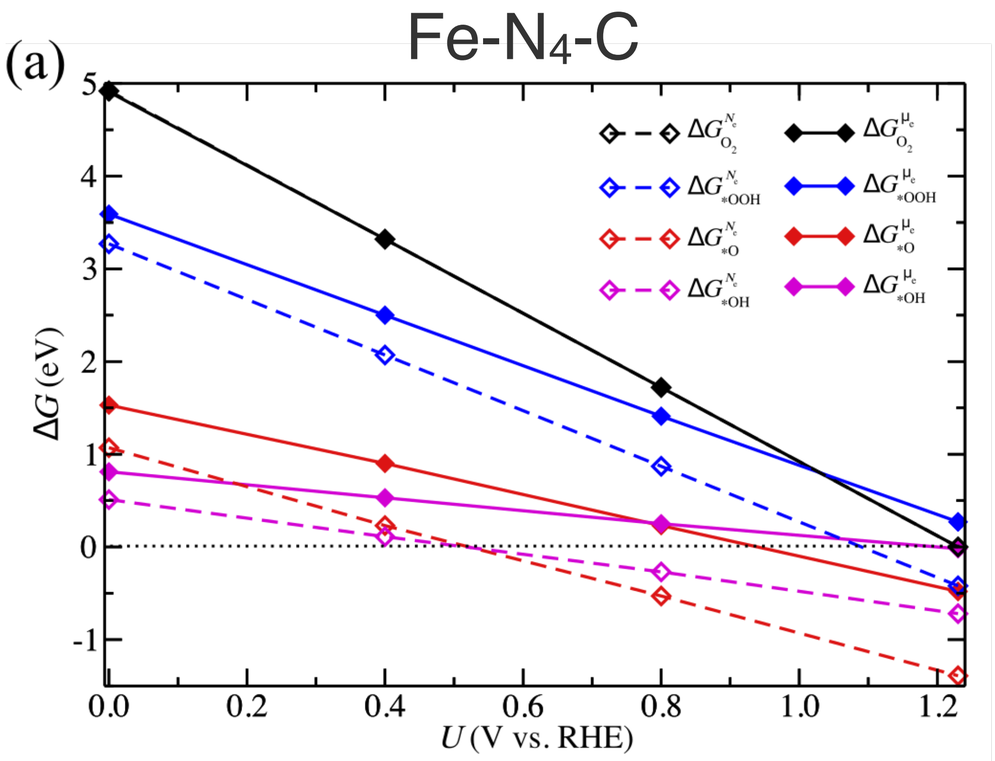
Free energy diagrams of Fe-N_4-C and Co-N_4-C from constant-*N* and constant-μ calculations

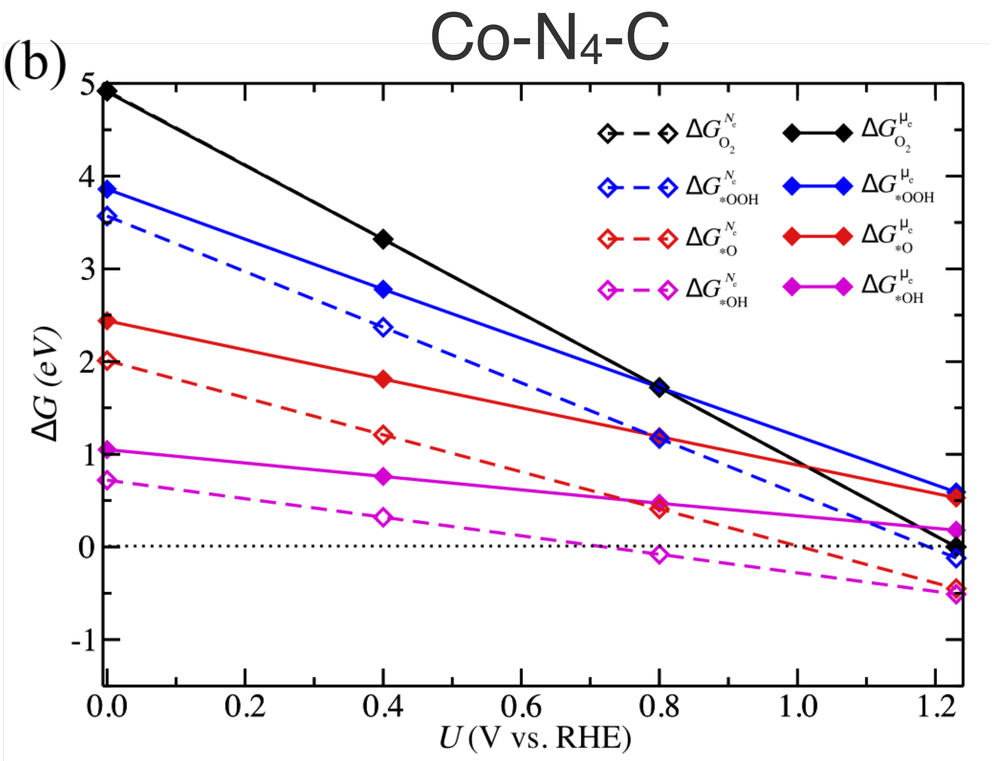
Free energy diagram from and constant-*N* constant-*μ*



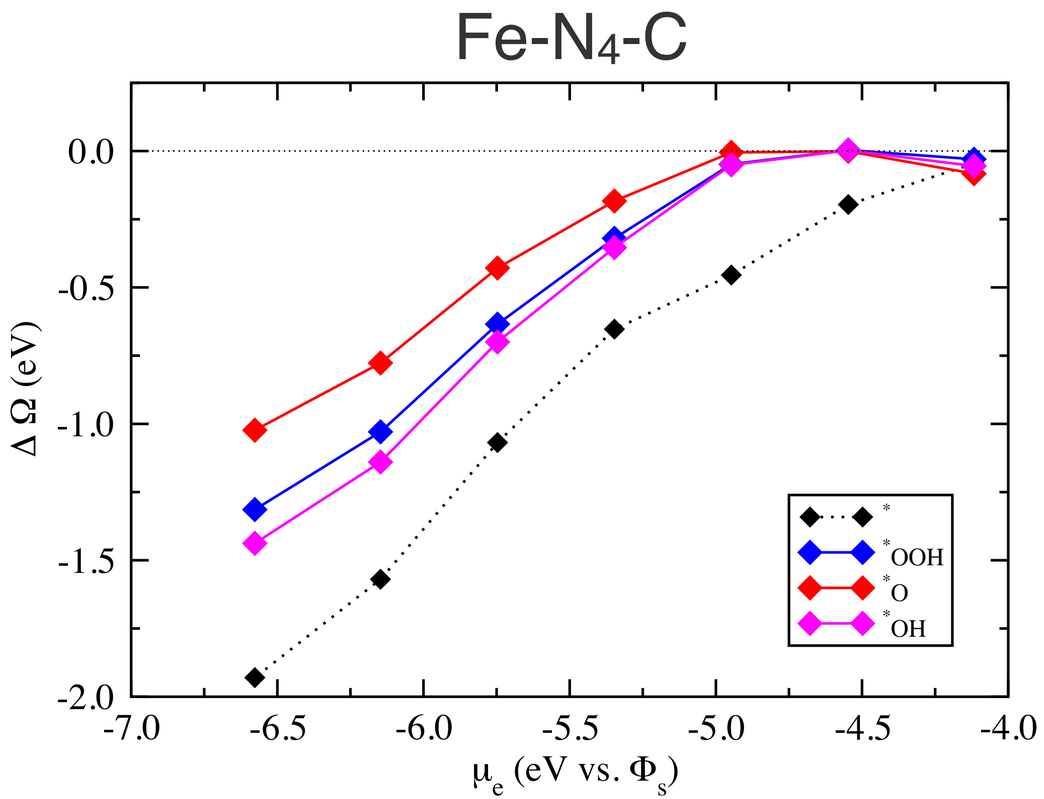
Free energies and granpotentials of Fe-N_4-C and Co-N_4-C

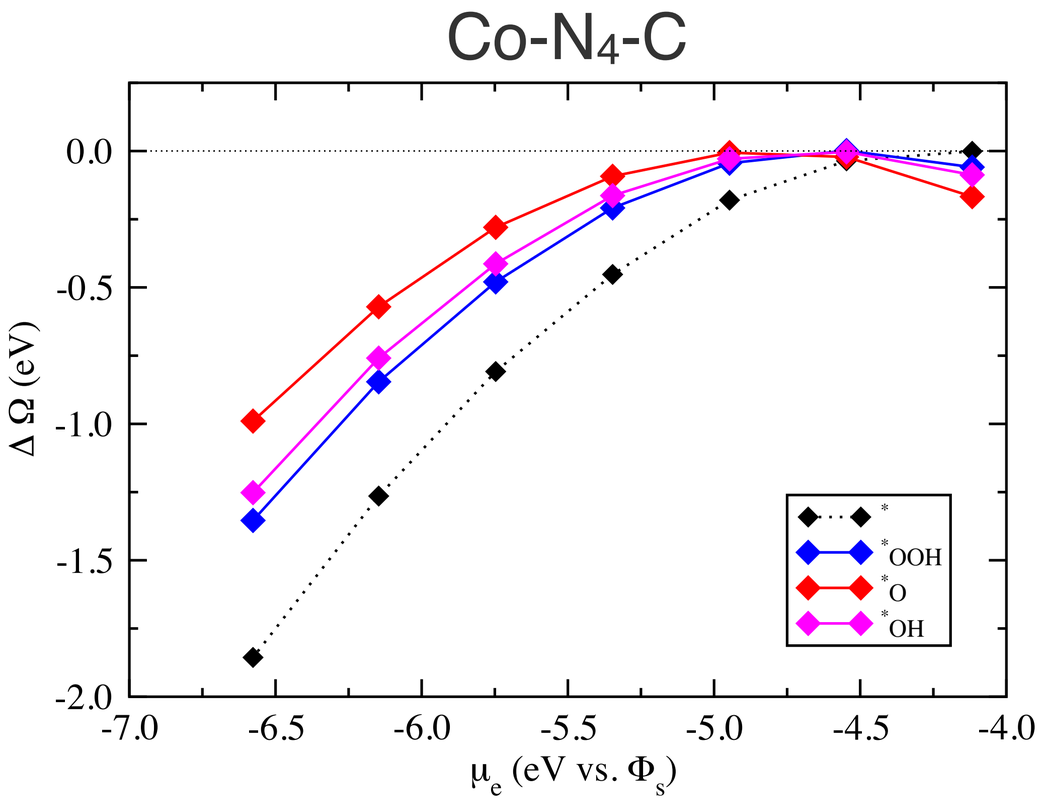
Free energies of the reaction intermediates



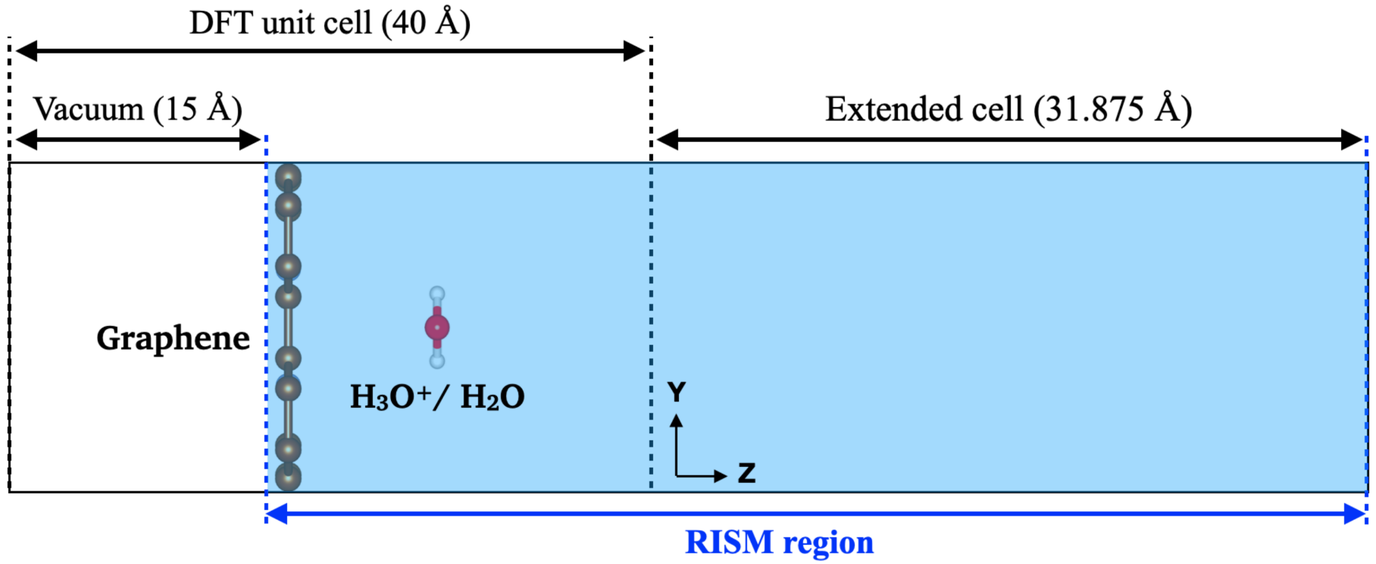


Grandpotentials

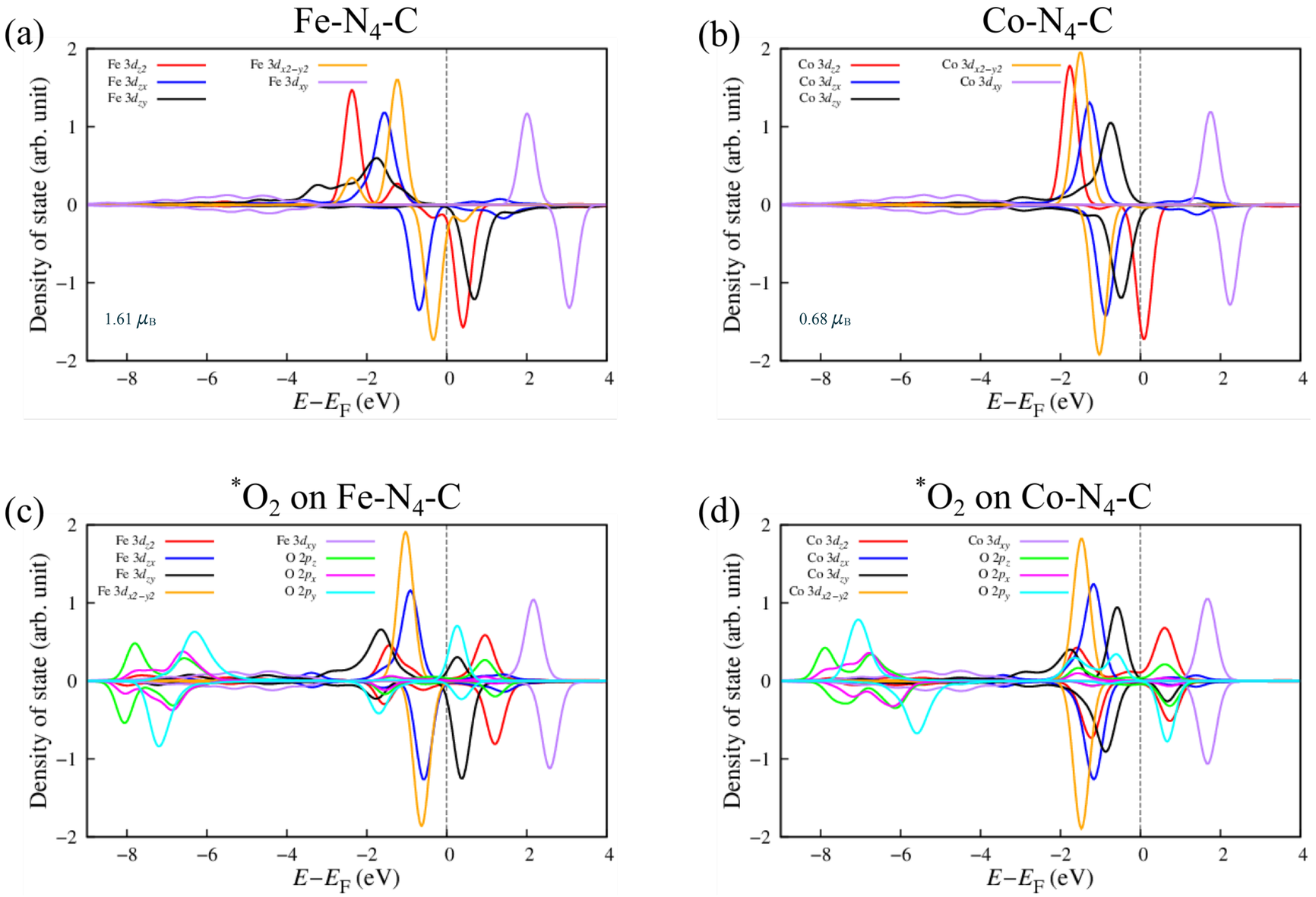




Simulation cell



Electronic structures



Effect of Hubbard *U* on the reaction free energies, potential determining steps and overpotentials

Adsorption free energies

	***U* = 0 eV**	***U* = 2 eV**
Fe-N_4-C (V)		
ΔG_{*OOH}	3.66	4.14
ΔG_{*O}	1.37	2.27
ΔG_{*OH}	0.71	1.03
Co-N_4-C (V)		
ΔG_{*OOH}	3.99	4.31
ΔG_{*O}	2.35	2.64
ΔG_{*OH}	1.01	1.32

PDS and Overpotential

	***U* = 0 eV**	***U* = 2 eV**
Fe-N_4-C (V)		
PDS	*O → *OH	*OOH → *O
Lim. potential	0.66	0.77
Overpotential	0.56	0.46
Co-N_4-C (V)		
PDS	O_2 → *OOH	*OOH → *O
Lim. potential	0.93	0.60
Overpotential	0.30	0.60

Effect of Hubbard *U* on the electronic structures