Structure & Reactivity of IrOx Nanoparticles for the Oxygen Evolution Reaction in Electrocatalysis: An Electronic Structure Study

Dr. Kalishankar Bhattacharyya

Molecular Theory and Spectroscopy
Max-Planck-Institut für Kohlenforschung

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Electrochemical Redox Reaction

Acidic conditions

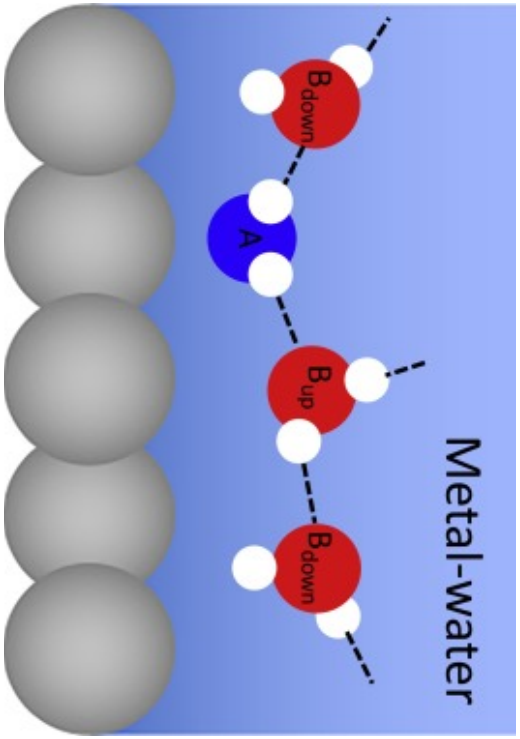
$$A + nH^+ + ne^- \rightleftharpoons B$$

Alkaline conditions

$$A + nH_2O + ne^- \rightleftharpoons B + nOH^-$$

- hydrogen oxidation reaction
- hydrogen evolution reaction
- oxygen evolution reaction
- oxygen reduction reduction
- carbon dioxide electro reduction

Electrochemical interface



Combine density functional theory with
Thermodynamic concepts

→ Chemical potentials

$$\mu_a = \frac{\partial G}{\partial n_a}$$

Gibbs free energy

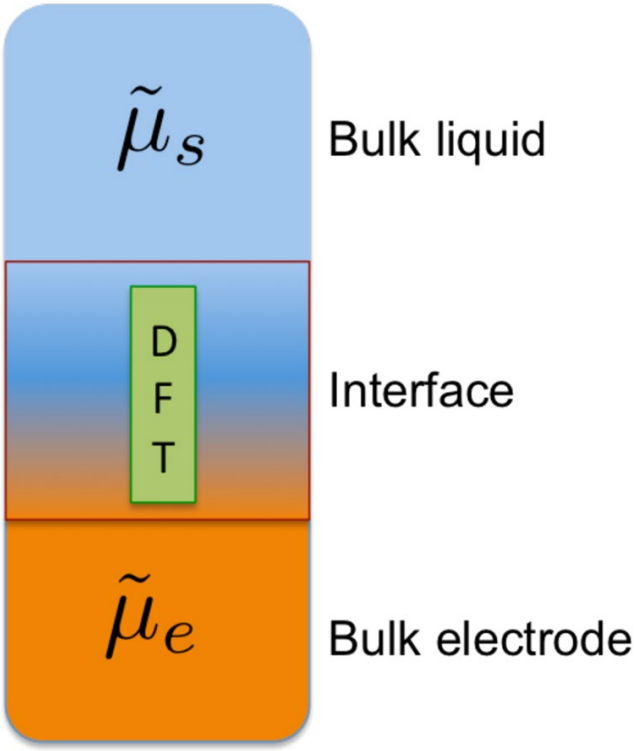
Number of atoms of species *a*

Chemical potentials allows us to compute the relevant structural entities separately

(divide and conquer)

Major challenge

Electrochemical interface at fixed electron μ_e and solvent/electrolyte μ_s chemical potentials.



Electrocatalytic performance controlled by

- Electrolyte composition
- Electrode potential

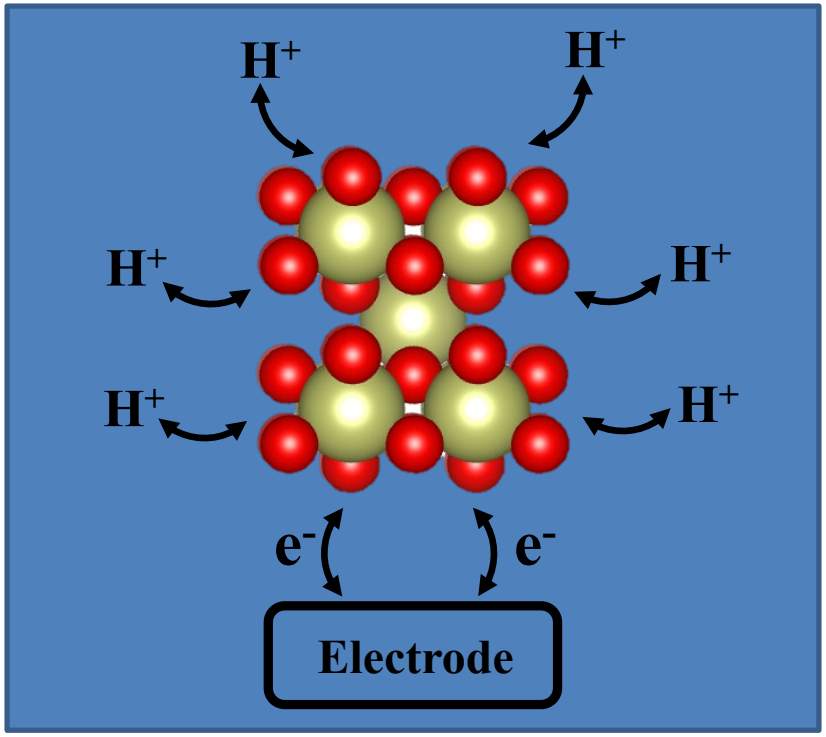
Can we address this in DFT calculations?

Fixed potential electronic structure calculation

Agenda

- **Computational model for description the electrochemical setup**
- **Simple method to calculate the solution-phase free energies of electrocatalysts**
- **Computational potential-pH diagrams as a descriptor for structure identification**
- **Applications to OER electrocatalyst.**

Computational model for description the electrochemical setup

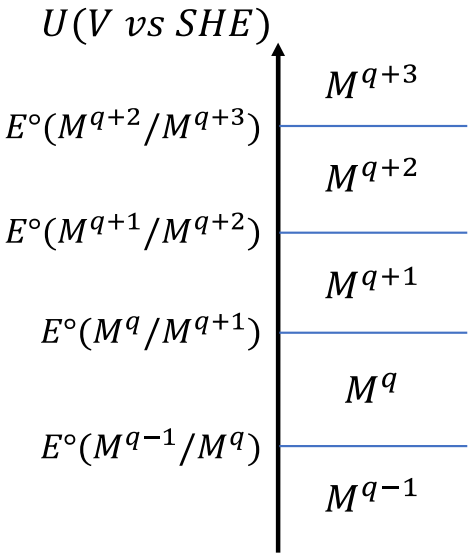


- Amorphous cluster structure
- PBE-D3 and B3LYP functionals for geometry optimization
- Implicit CPCM model

- Exchange of electrons and protons with bath (electrode/solvent).
- Charged state of the cluster tuned by potential and pH.

Computational model for description the electrochemical setup

❖ Calculations of stable charged state at specific potential: Constant Potential



➢ **Redox reaction:**

$$M^q + e^- \rightleftharpoons M^{q-1}$$

- optimizations of each charged state
- Energy difference between charged state yields the energy of the transferred electrons.

➢ **Potential**

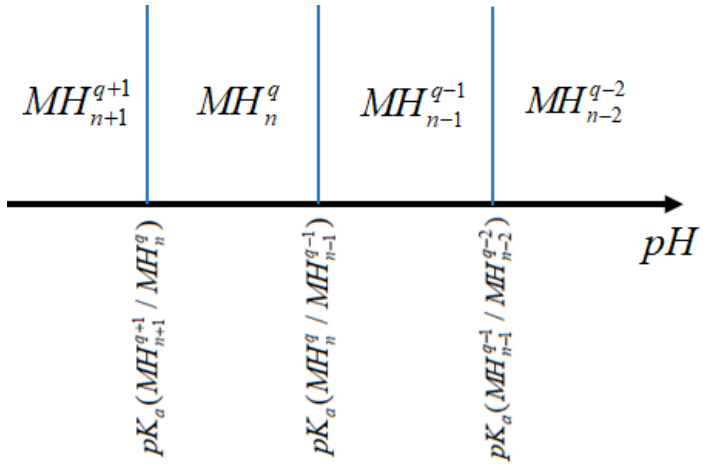
$$E^0 = \mu^0(M^{q-1}) - \mu^0(M^q) - 4.28\ (eV)$$

Computational model for description the electrochemical setup

❖ Proton transfers: Effect of pH

➢ **Acid-Base reaction:**

$$MH_{n-1}^{q-1} + H^+ \rightleftharpoons MH_n^q$$



➢ **Reaction free energy calculation**

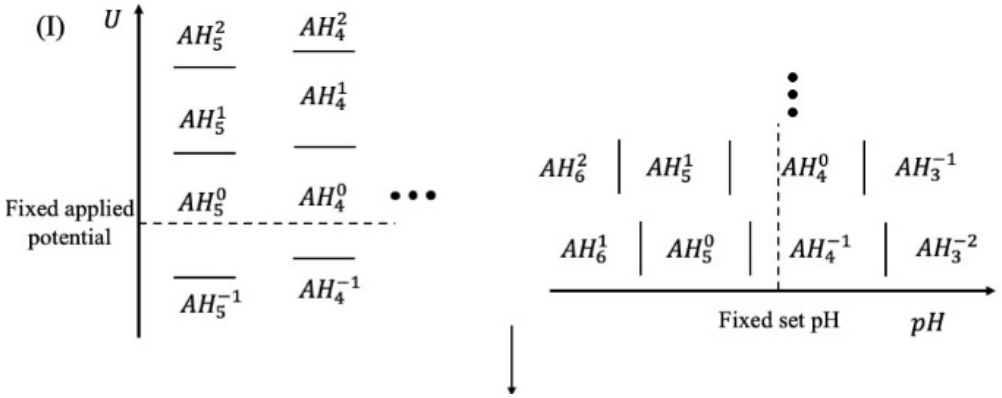
$$\Delta G = \mu^0(MH_{n-1}^{q-1}) + \mu^0(H_s^+) - \mu^0(MH_n^q) + RT\ln\frac{[MH_{n-1}^{q-1}][H_s^+]}{[MH_n^q]}$$

➢ **Calculation of pK_a**

$$pK_a = \frac{\mu_s^0(A^-) + \mu_{eff}^0(H^+) - \mu_s^0(AH)}{k_b T\ln(10)}$$

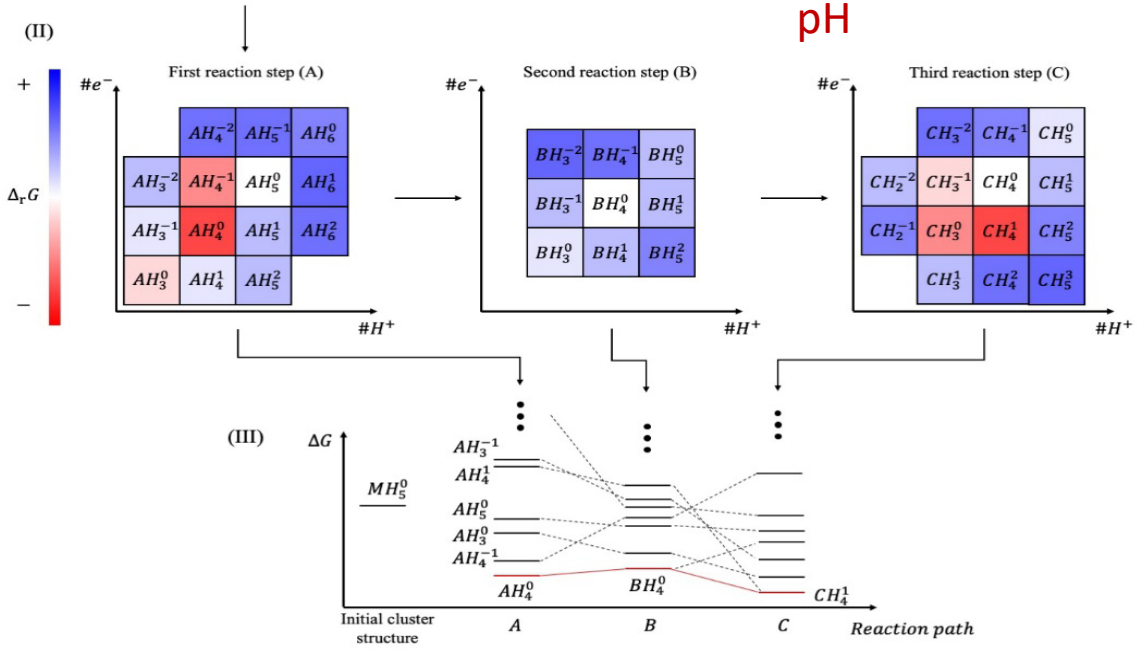
Set of reference system is taken with known experimental pKa to compute the effective chemical potential $\mu_{eff}^0(H^+)$

2D phase diagram with U and pH



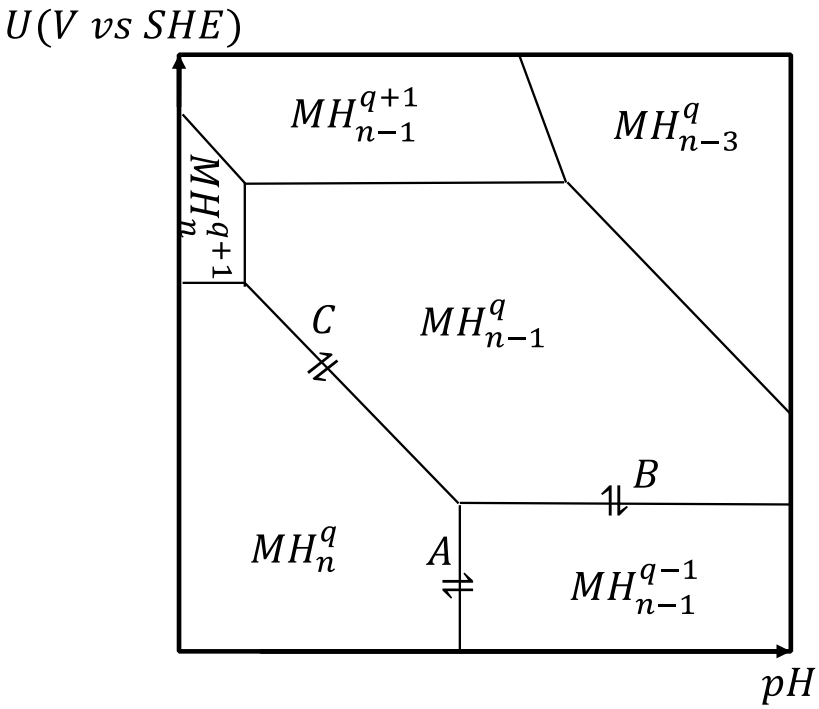
$$\Delta G_{AH_5^0}(AH_n^q) = (\mu_{AH_n^q} - \mu_{AH_5^0}) + (5-n)\mu_{H^+} - (5-n)RT\ln(10)\,pH - (5-n-q)(4.28+U)$$

pH U



Potential-pH diagram

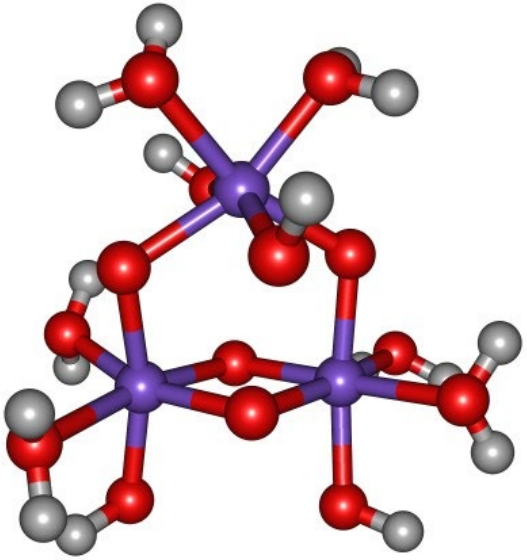
$$\Delta G_{AH_5^0}(AH_n^q) = (\mu_{AH_n^q} - \mu_{AH_5^0}) + (5-n)\mu_{H^+} - (5-n)RT\ln(10)\,pH - (5-n-q)(4.28+U)$$



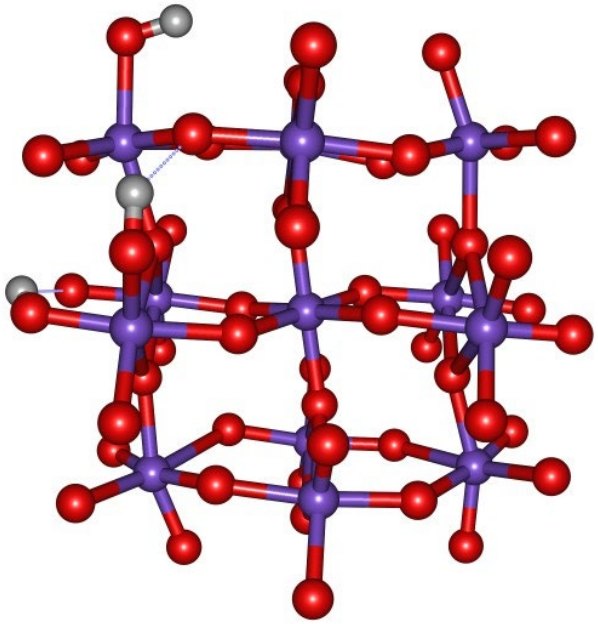
- Computational potential-pH diagrams as a descriptor for structure identification

IrO_x Electrocatalyst at Acidic Condition

❖ Cluster Approach



$Ir_3(O\mu_2)_4(OH\mu_1)_4(H_2O)_6$



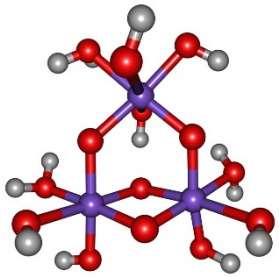
$Ir_{13}(O\mu_1)_{29}(O\mu_2)_{14}(O\mu_3)_6(OH\mu_1)_3$

- Cluster model is chosen for describing local phenomena i.e. interaction on catalytically active sites.

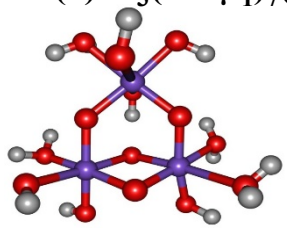
- Cluster approach is also efficient for modelling defect sites which is crucial for understanding the experimental findings.

Bhattacharyya et al. JPCC, 2021, 125, 4379-4390

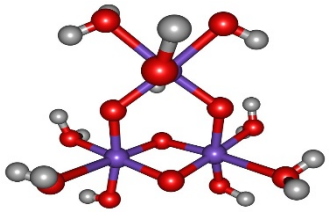
Potential-pH Diagram of Small Cluster



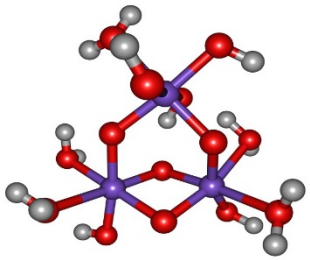
(4) $Ir_3(OH\mu_1)_7(H_2O)_3$



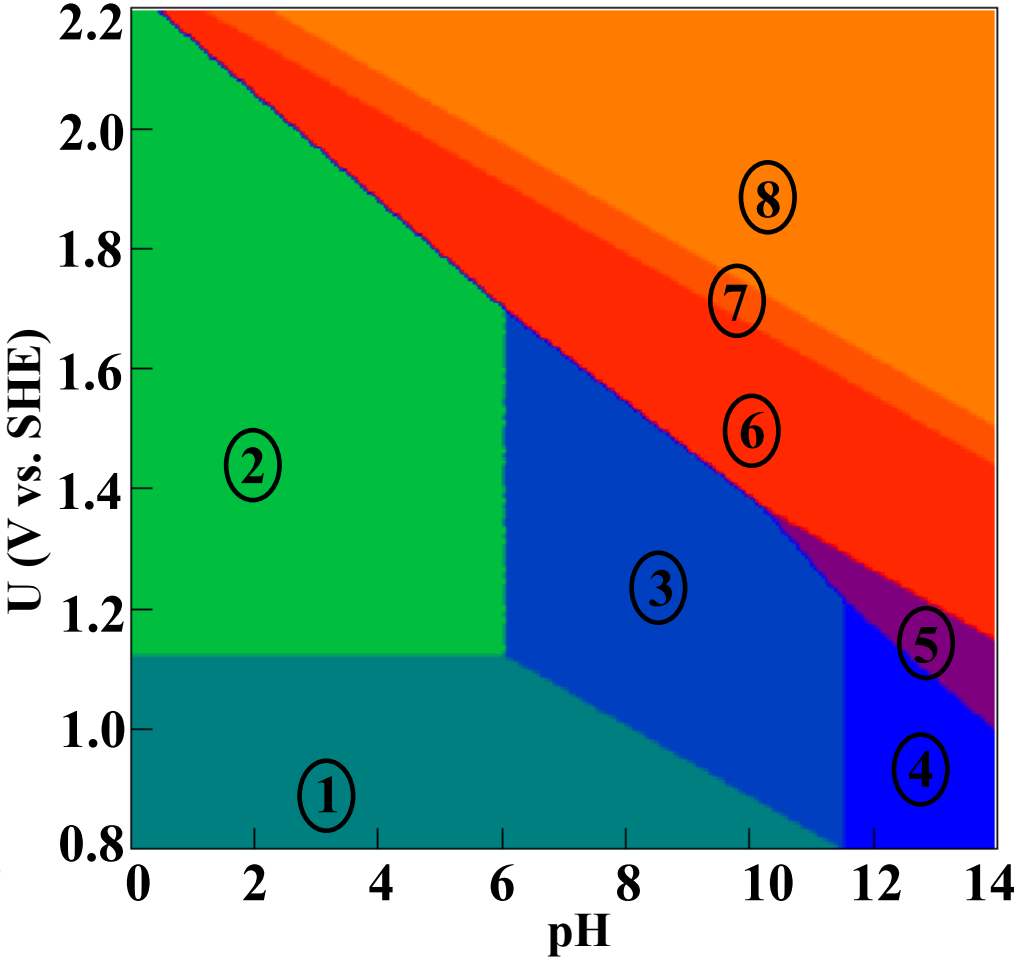
(3) $Ir_3(OH\mu_1)_6(H_2O)_4^+$

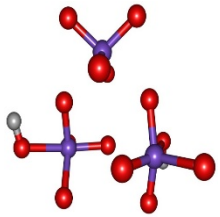


(2) $Ir_3(OH\mu_1)_5(H_2O)^{2+}_5$

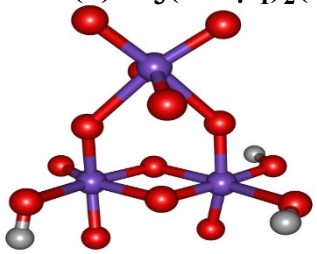


(1) $Ir_3(OH\mu_1)_5(H_2O)^+_5$

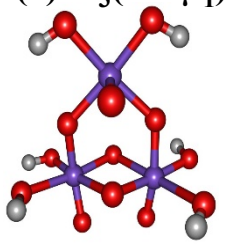




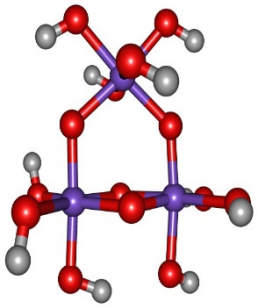
(8) $Ir_3(OH\mu_1)_2(O\mu_1)_8^-$



(7) $Ir_3(OH\mu_1)_3(O\mu_1)_7^-$

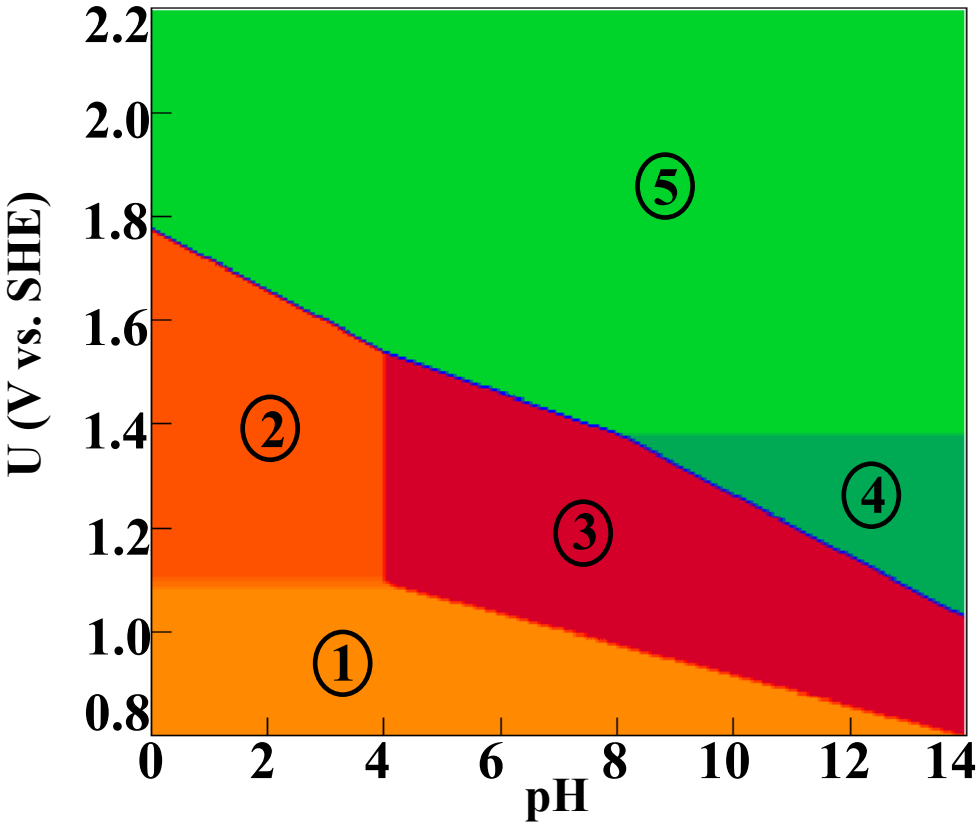


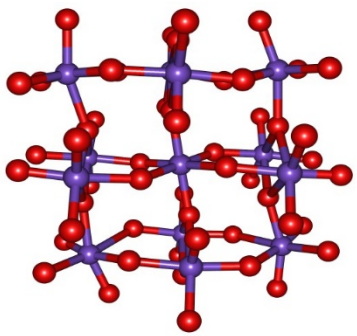
(6) $Ir_3(OH\mu_1)_6(O\mu_1)_4^-$



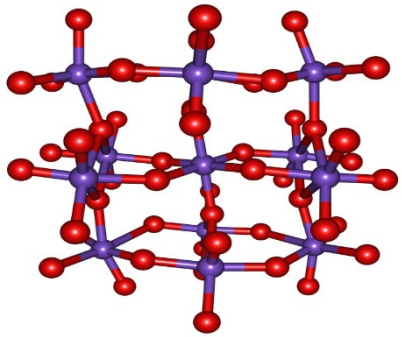
(5) $Ir_3(OH\mu_1)_{10}^-$

Potential-pH Diagram of Larger Cluster

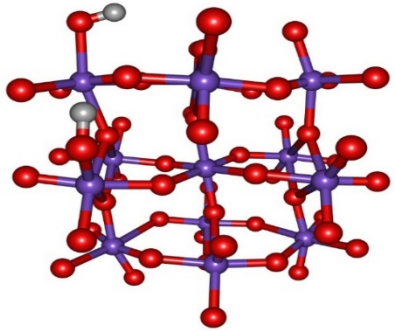




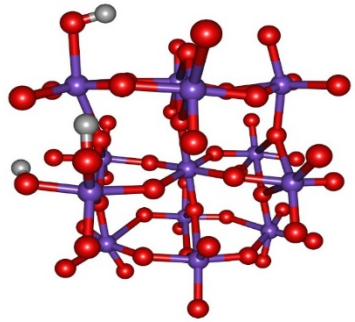
(5) $Ir_{13}(O\mu_1)_3^{3-}$



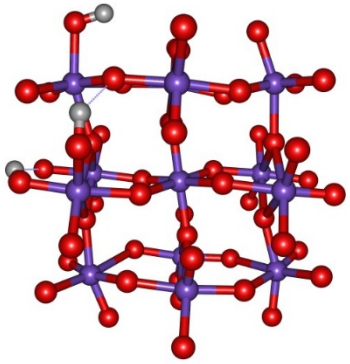
(4) $Ir_{13}(O\mu_1)_3^{4-}$



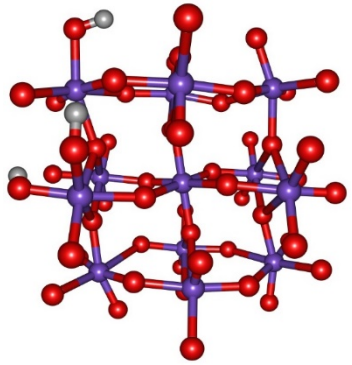
(3) $Ir_{13}(OH\mu_1)_3^{4-}$



(2) $Ir_{13}(OH\mu_1)_3^{3-}$

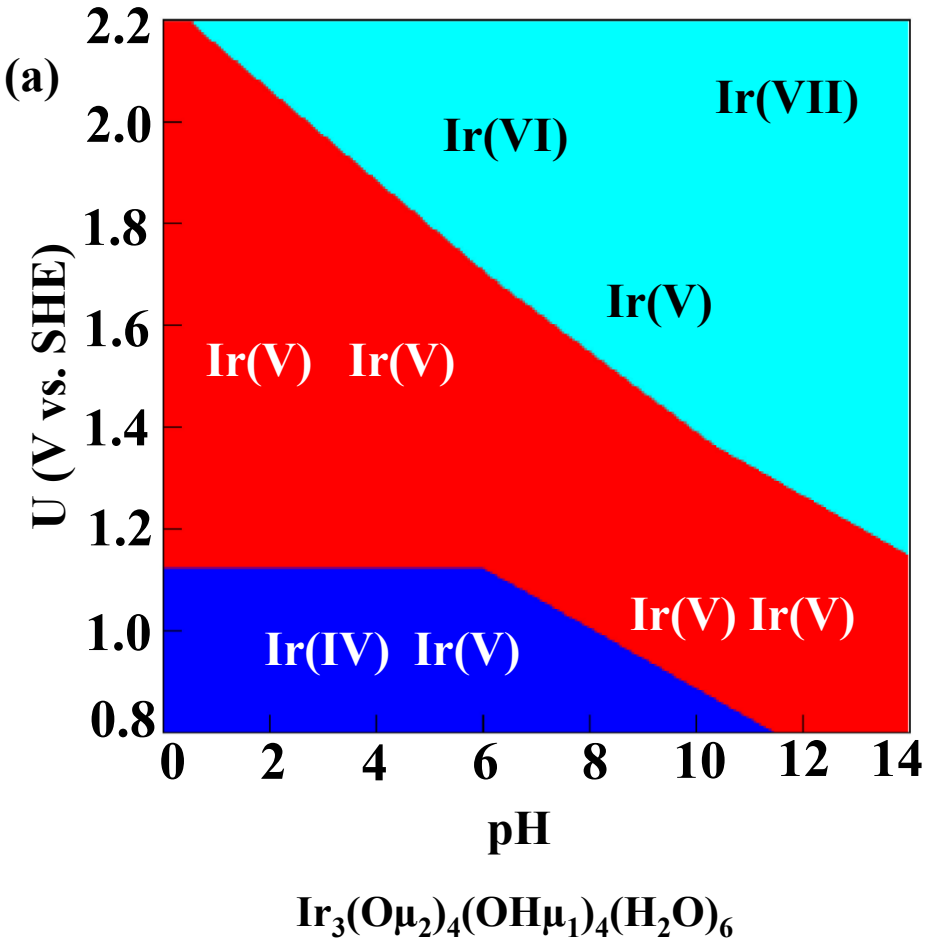


Calculations on larger cluster confirms the presence of protons in acidic region.

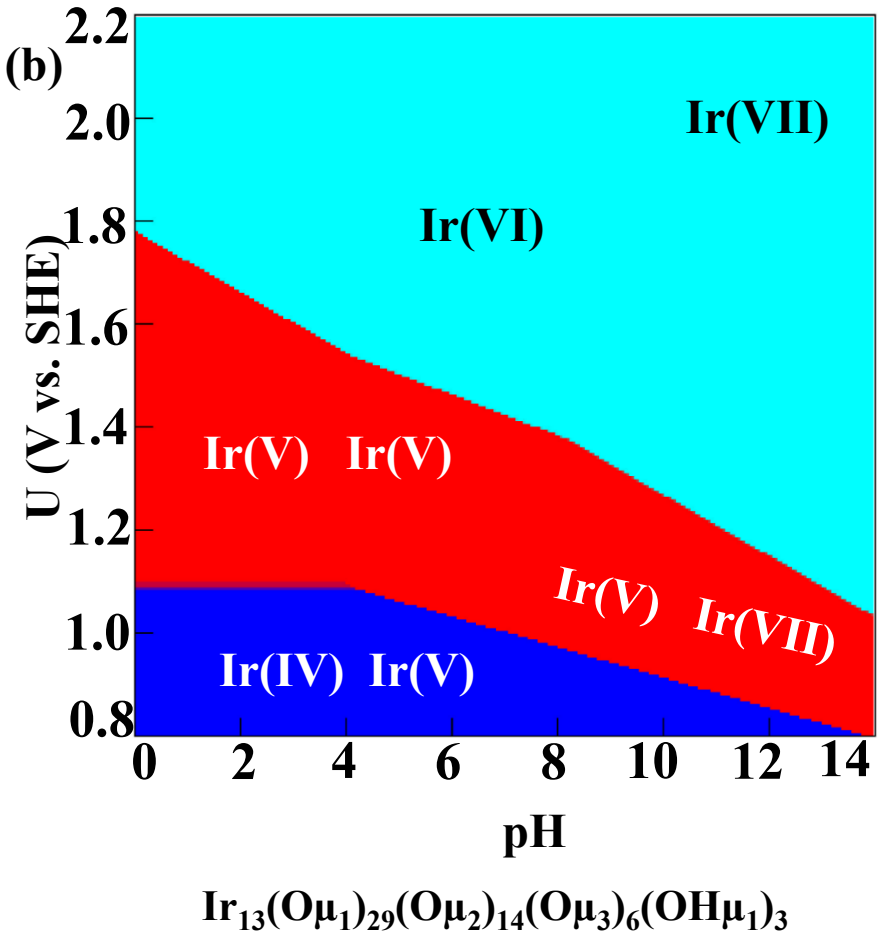


(1) $Ir_{13}(OH\mu_1)_3^{5-}$

Oxidation States of Ir Center



$Ir_3(O\mu_2)_4(OH\mu_1)_4(H_2O)_6$



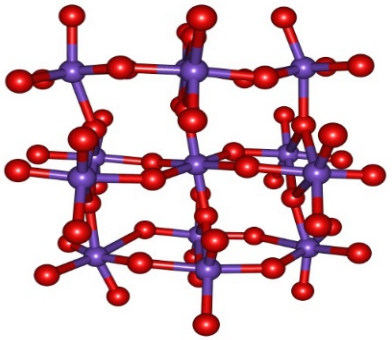
$Ir_{13}(O\mu_1)_{29}(O\mu_2)_{14}(O\mu_3)_6(OH\mu_1)_3$

- Mixed oxidation state arises in the OER potential region.
- High valent oxidation states hints the possible dissolution process at high potential.

Mayrhofer et al. Angew. Chem. 2018, 57, 2488-2491

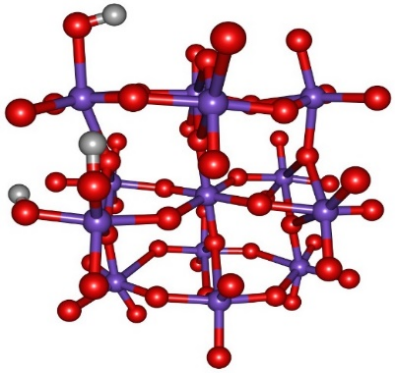
Reaction Mechanism of O-O Bond Formation

Potential U~1.90 V



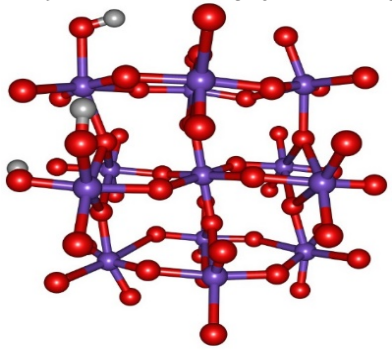
(3) $Ir_{13}(O\mu_1)_{29}(O\mu_2)_{14}(O\mu_3)_6(O\mu_1)_3^{3-}$

Potential U~1.54 V

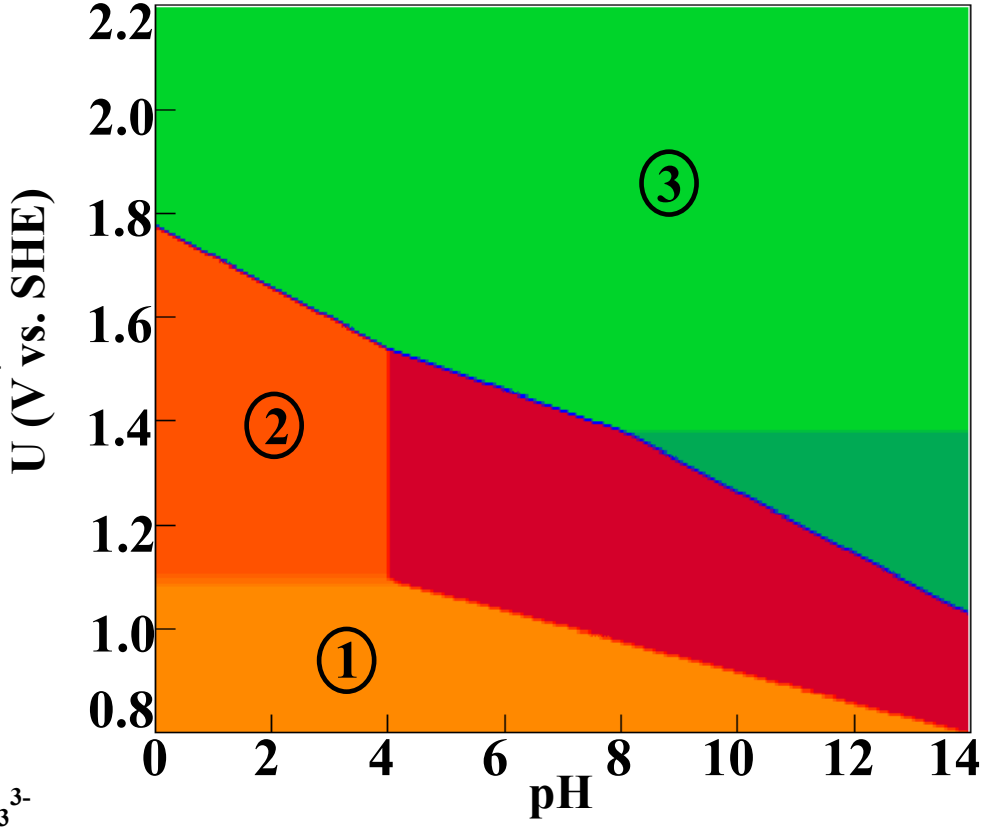


(2) $Ir_{13}(O\mu_1)_{29}(O\mu_2)_{14}(O\mu_3)_6(OH\mu_1)_3^{3-}$

Potential U~1.10 V



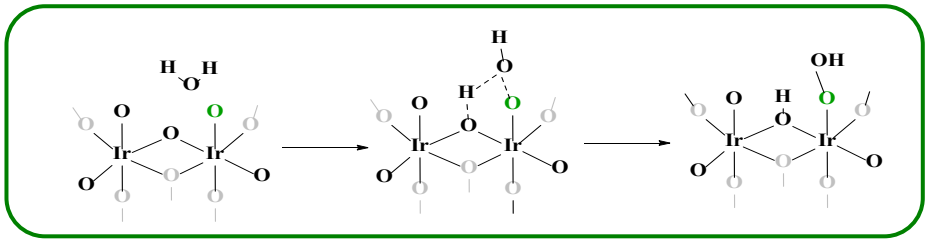
(1) $Ir_{13}(O\mu_1)_{29}(O\mu_2)_{14}(O\mu_3)_6(OH\mu_1)_3^{5-}$



Mechanistic Pathway for O-O Bond Formation

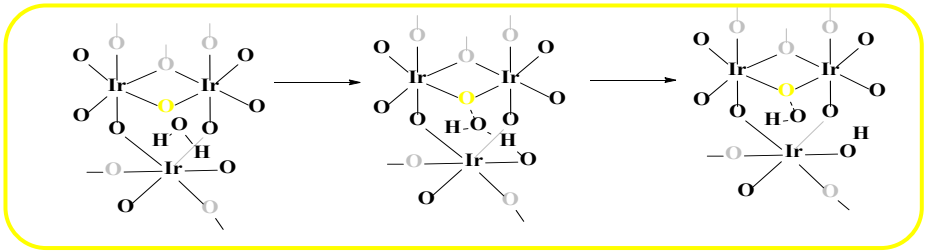
❖ **Nucleophilic Addition of Water**

(a)



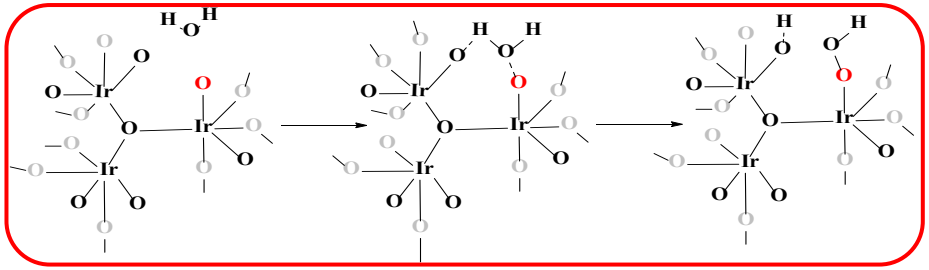
$O^{(1)}_{\mu 1}$ pathway

(b)



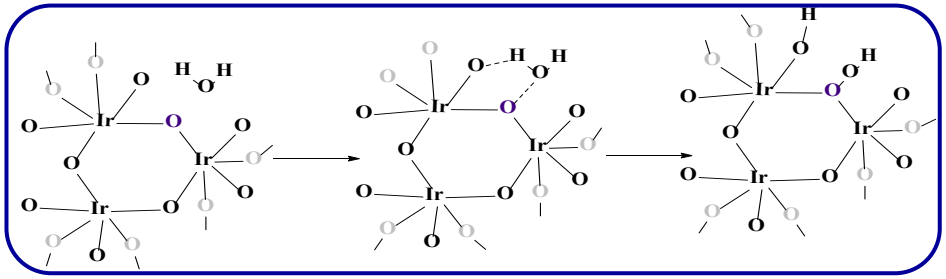
$O^{(1)}_{\mu 2}$ pathway

(c)



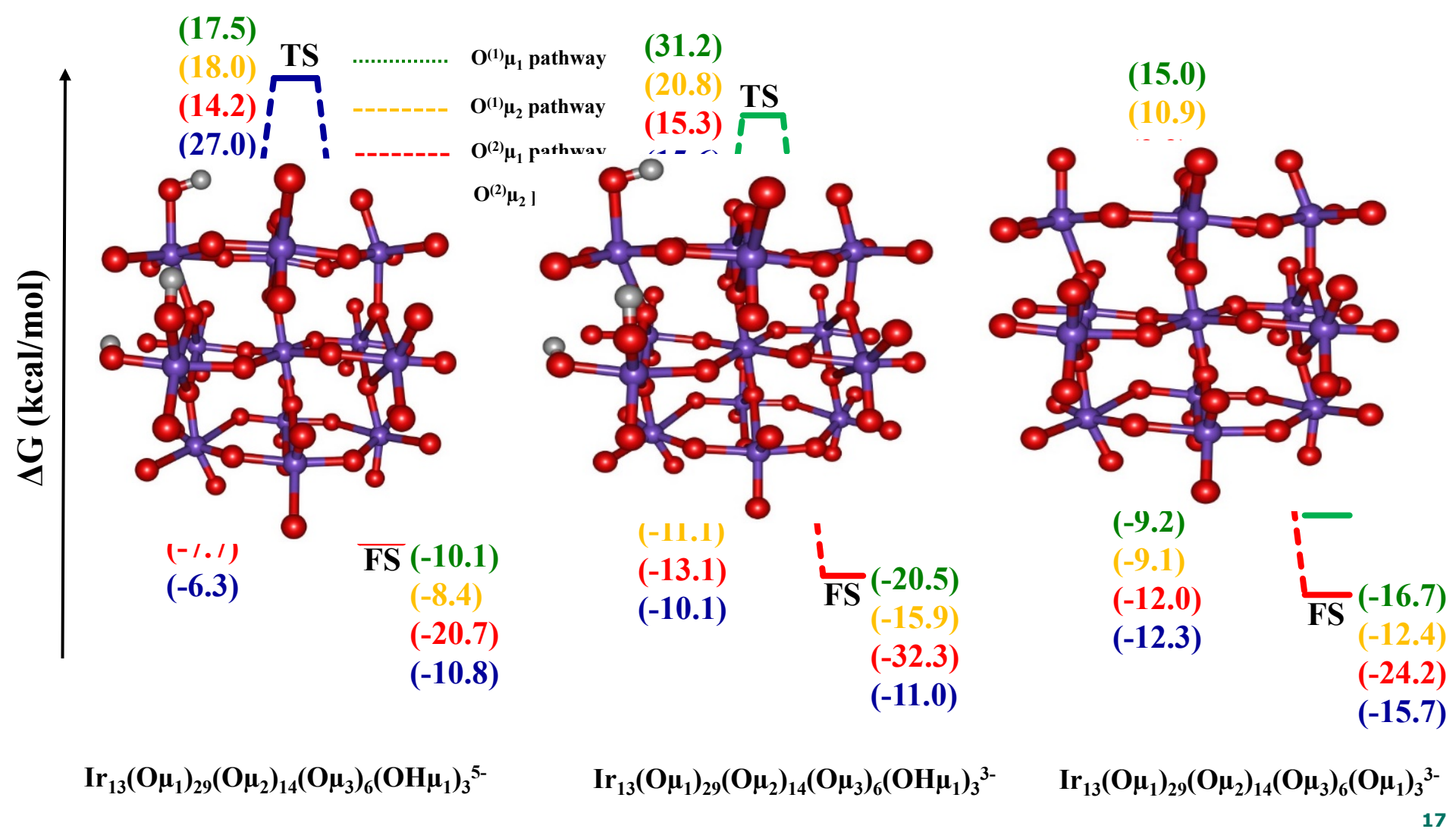
$O^{(2)}_{\mu 1}$ pathway

(d)



$O^{(2)}_{\mu 2}$ pathway

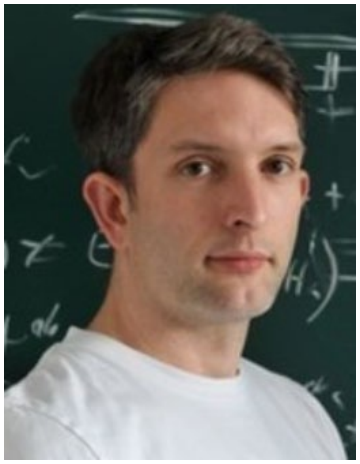
Potential vs. Energy Profile



Take Home Message

- New methodology to describe the structural analysis under electrochemical conditions.
- In acidic region with low potential region, cluster structure are mostly protonated; covered by aqua and hydroxyl group.
- Deprotonated structures with possible exotic species arises at high potential region.
- Electronic structure analysis reveal the mixed oxidation state exist in the OER potential region.
- O-O bond formation step are significantly reduces from low potential to high potential regime.

Acknowledgement



Dr. Alexander A. Auer

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Stiftung/Foundation

Max-Planck-Institut
für Kohlenforschung

Email: ksb@kofo.mpg.de