Atomistic Simulations of Hydrogen Production Kinetics at Novel Fuel Cell Electrodes

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OFFICE OF UNDERGRADUATE RESEARCH

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Background

- **Electrocatalysts**, such as Platinum (Pt), are used to minimize the overpotential for electrochemical reactions, i.e. **hydrogen evolution reaction (HER).**
- **Iron phosphides (Fe_xP)** were recently identified as one of the more promising transition metal phosphides (TMPs) that can substitute Pt at a much lower cost.

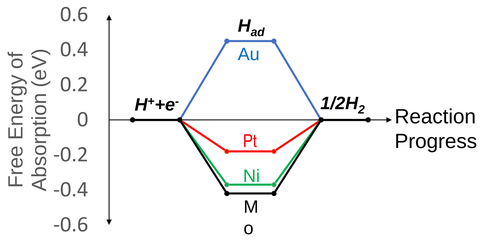


Figure 1. Reaction coordinate of different metal in the progress of forming half hydrogen molecules from hydrogen ions.[1]

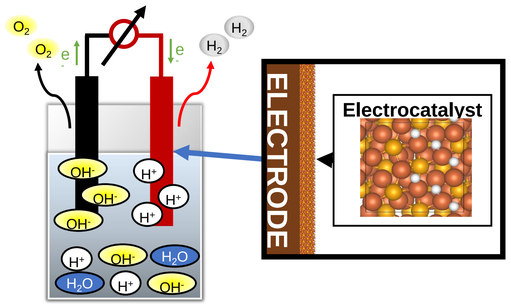


Figure 2. Fe_xP electrocatalyst is embedded on the cathode of electrolysis (water splitting) process.

- Preliminary thermodynamic analysis shows that Fe_xP electrocatalyst with higher concentration of Iron (Fe) outperforms Fe_xP with lower concentration of Fe.
- The kinetics of hydrogen recombination was investigated on six Fe_xP (x = 1,2,3) surface facets using **density functional theory (DFT)** to further understand their activity.

Methodology

MobaXterm
An enhanced terminal for remote computing
- Use text editors, such as (VI Editor or Emacs) to create scripts
- Manage configuration or script files in an organized manner

Python

Atomic Simulation Environment (ASE)
A set of modules written in Python programming language [2]
- Set up, manipulate, run, visualize and analysing atomistic simulations
- Set up Vienna ab initio Simulation Package (VASP) calculation

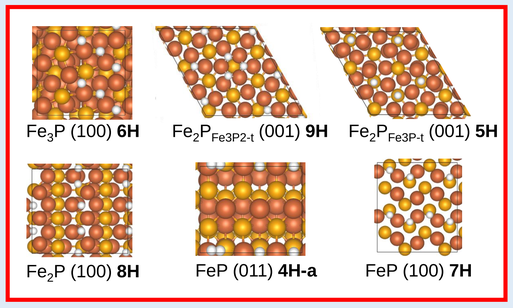
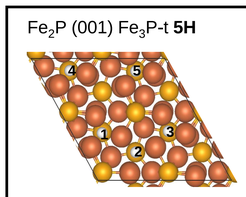


Figure 3. Each Fe_xP surface with specific hydrogen coverage near to zero differential Gibbs free binding energy of hydrogen (ΔG_H) are investigated.

Python

VASP
A total energy code based on DFT
- Perform geometry optimization to obtain the ground state atomic configuration of the model with the lowest energy
- Implement nudged elastic band (NEB) algorithm to find saddle points, i.e. activation energy (E_a) barrier, between reactants and products[3]

By using ASE and VASP, we evaluated the ΔE or energy change for different combination of absorbed hydrogen ions (H*) to form $H_{2(g)}$ and identify the easiest removable H_2 on each Fe_xP surface.



Label	Combination		ΔE
T1	1	2	0.12
T2	**2**	**3**	**0.11**
T3	1	4	0.36
T4	3	5	0.51
T5	1	5	0.53
T6	2	5	0.13
T7	4	5	0.53
T8	**2**	**4**	**0.11**

Figure 4. The ΔE for each term (T) consist of a pair of hydrogen combination on the Fe_xP surface.

We interpolate five images between the initial state and final state to create an initial guess for the reaction pathway. Then, we calculate each image's energy and force to find the E_a.

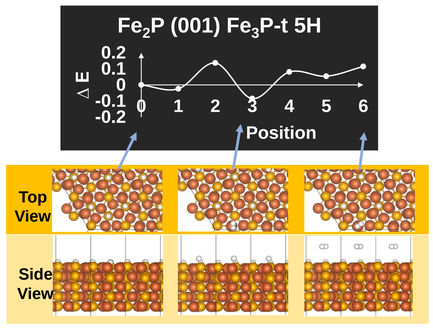


Figure 5. The ΔE on the $Fe_2P_{Fe3P\text{-}terminated}$ surface from the initial position (0) to the final position (6).

Results and Discussion

- As ΔG_H reaches zero, the adsorption of protons on Fe_xP surfaces and the desorption of H_2 are both expected to be facile.
- From Figure 6, we selected Fe_xP surfaces for the number of hydrogen coverage that satisfy the necessary criterion $\Delta G_H \approx 0$ kJ/mol and analyzed the recombination kinetics of H_2 .
- The specifics surfaces used are:
  - **Fe_3P:**
    (100) – 6H and 7H
  - **Fe_2P:**
    (011) Fe_3P_2-t – 9H and 10H
    (011) Fe_3P-t – 5H and 6H
    (100) – 8H and 9H
  - **FeP:**
    (011) Fe-t – 3H and 4H
    (011) P-t – 1H
    (100) – 7H
- From VASP calculation, we found the best hydrogen combination pairs on each Fe_xP surface with the most negative Δ E to form H_2 much easier.

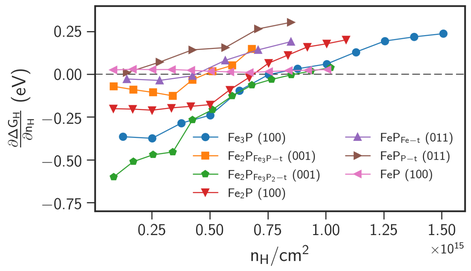


Figure 6. The ΔG_H for seven Fe_xP surfaces with different stoichiometry and termination as function of hydrogen coverage. [4]

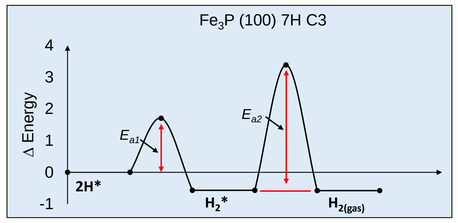


Figure 7. The graph of energy change against reaction progress. The *Ea* for surface hydrogen recombination is lower than for hydrogen pair removal.

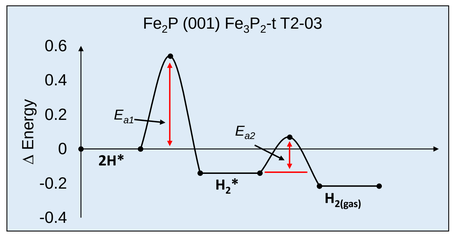


Figure 8. The graph of energy change against reaction progress. This figure shows a reverse E_a requirement that is different from Figure 7.

- From the NEB calculation, we analysed the energy of each transition state from 2 H* to H_2* and form $H_{2(g)}$.
- The first activation energy (E_{a1}) is needed for a hydrogen pair (2H*) to relocate and combine together on the surface.
- The second activation energy (E_{a2}) is required for the specific surface hydrogen pair (H_2*) to dissociate away from the surface as hydrogen gas (H_2).

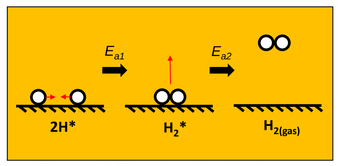


Figure 9. The simplified hydrogen recombination reaction steps.

- We discovered a possible reaction intermediate, a surface hydrogen molecule (H_2*), with lower energy that formed on the surface before H_2 desorption.

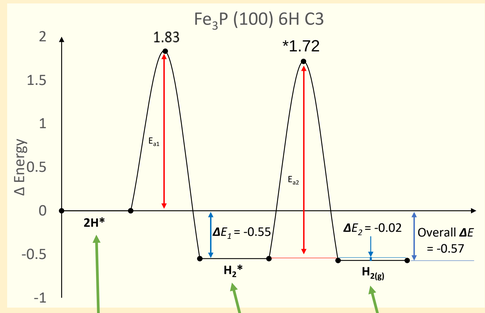


Figure 11. The ΔE on the Fe_3P surface for hydrogen coverage number of 6 (3rd combination) from the initial position (0) to the final position (6). The illustration below graph shows the top and side view for an easier understanding.

Table 1. The reaction intermediate is discovered from the NEB calculation of $Fe_2P_{Fe3P\text{-}terminated}$ surface in Figure 5. We separated NEB calculation into two parts and recalculated them to find two E_a.

	Surface	H Coverage	H_2 Combination	E_{a1}	ΔE_1	E_{a2}	ΔE_2	Overall ΔE
Fe_3P	(100)	6H	C3	1.83	-0.55	*1.72	-0.02	-0.57
Fe_3P	(100)	7H	C3	1.70	-0.57	3.38	-0.01	-0.58
Fe_2P	(001) Fe_3P_2-t	9H	T2-03	0.54	-0.14	0.07	-0.08	-0.22
Fe_2P	(001) Fe_3P-t	5H	T8-03	1.05	-0.09	0.18	0.14	0.05
Fe_2P	(100)	8H	T12-04	0.46	0.19	*-0.01	-0.73	-0.54
FeP	(011)	4H-a	C3	0.59	-0.31	*0.33	0.28	-0.04
FeP	(100)	7H	C7	*5.85	0.27	0.21	0.18	0.45

Conclusions

- A stable reaction intermediate, i.e. a surface hydrogen molecule (H_2*) is predicted to form on the Fe_xP surface before desorption of H_2.
- From our preliminary analysis, Fe_2P and FeP have better HER kinetics, which we tentatively attribute to their lower metal concentration allowing for higher H mobility.
- Further studies are needed to understand the contradictory result between the preliminary thermodynamic analysis and atomistic simulation exploration.

Acknowledgements

Thanks to the Summer Undergraduate Research Fellowship (SURF) program for this remarkable experience and the support for this research project. A special thanks to my faculty mentor, Dr. Grabow, for the research opportunity and Hari for all the advices and guidance throughout this summer program. Thank you to Center for Advanced Computing and Data Science (CACDS) for providing the necessary computational resources for this project.

References

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[4] D. E. Schipper et al., "Effects of Catalyst Phase on the Hydrogen Evolution Reaction of Water Splitting: Preparation of Phase-Pure Films of FeP, Fe2P, and Fe3P and their Relative Catalytic Activities", Chemistry of Materials, vol. 30(10), p. 3588-3598, 2018