Interaction of [NiFe] hydrogenases on a graphite electrode

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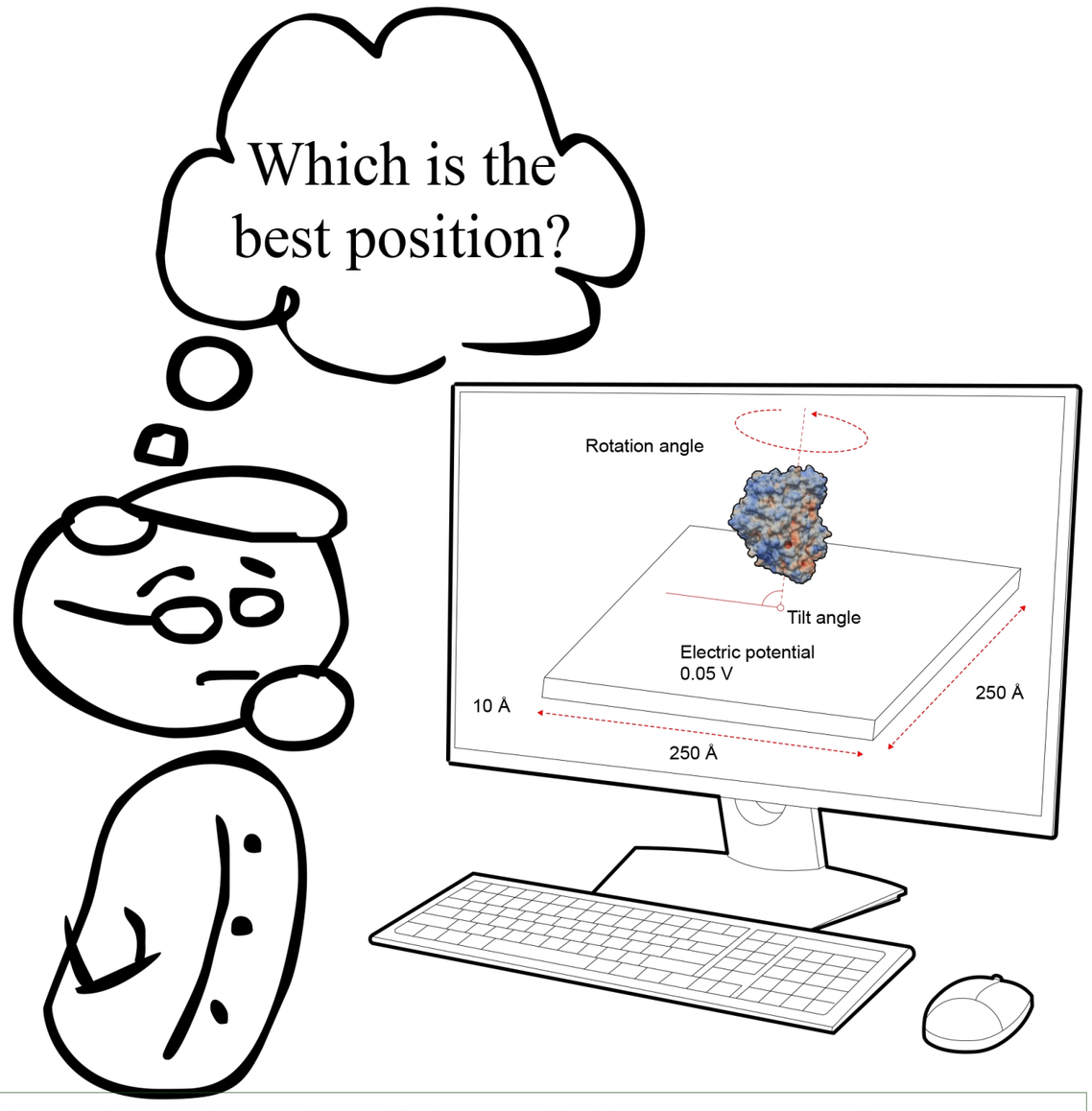
1. Introduction

Hydrogenases are a family of enzymes that have been studied by researchers in renewable energies in the last years, due their ability of catalyze the redox reaction of hydrogen:

$$2H^+ + 2e^- \rightleftharpoons H_2$$

This reaction indicates that hydrogenases could be used to produce hydrogen or electricity in electrochemical devices. Some studies have tried of immobilize these enzymes on the surfaces of electrodes with some grade of success [1], but better understanding of how this process occurs at atomic level is necessary, because the orientation of the enzyme with respect to the electrode surface is very important in order to ensure a good flux of electrons to the catalytic center of the enzyme.



2. Goal

The goal of this study is to determinate how the orientation of hydrogenase 1e3d can be influenced by the conditions applied on a graphite electrode. In order to determine the most favorable orientation that facilitates the flux of electrons from the electrode to the enzyme.

3. Procedure

In order to determine such orientation, computational simulations based in the Poisson-Boltzmann equation, in an implicit-solvent model were used to calculate and evaluate the total energy of the interaction of hydrogenase 1e3d (pdb code) on a graphite electrode using the PyGBe software[2]. **Total energy = Coulombic energy + Surface energy + Solvation energy.** The simulations considered as independent variables the: pH, salinity and electric potential.

4. Results

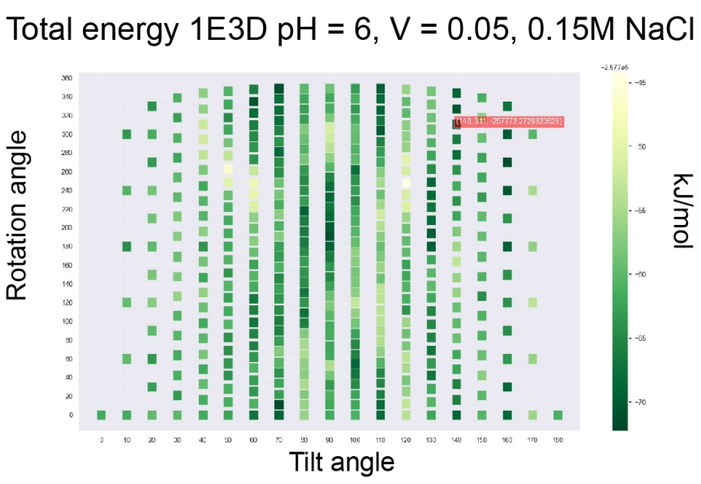


Figure 1. Values of total energy calculated by PyGBe for the hydrogenase at pH 6 and 0.05 V, each square represent the result of a calculation; deeper the color, lower the energy.

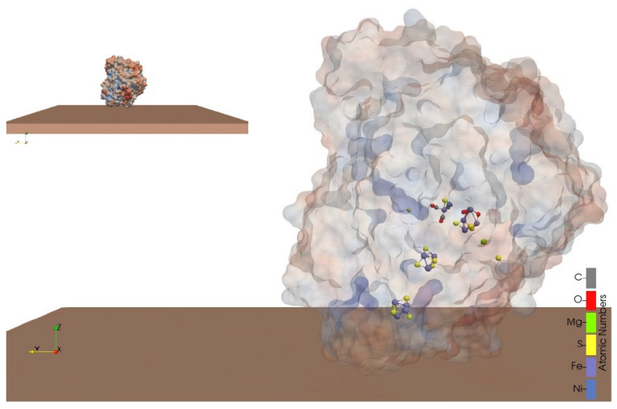


Figure 2. Representation of the position with the lowest total energy of the set of calculations done at pH 6 and 0.05 V. Under these conditions, the external FeS cluster was placed close to the surface of the electrode, this orientation is the most favorable for the flux of electrons towards the catalytic center of the hydrogenase.

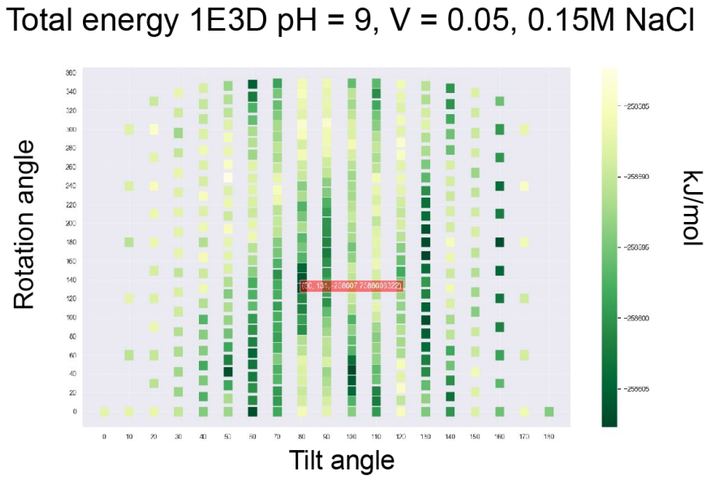


Figure 3. Values of total energy calculated by PyGBe for the hydrogenase at pH 9 and 0.05 V, each square represent the result of a calculation; deeper the color, lower the energy and highest its probability of occur such position, in this case a change of pH has flip up the enzyme.

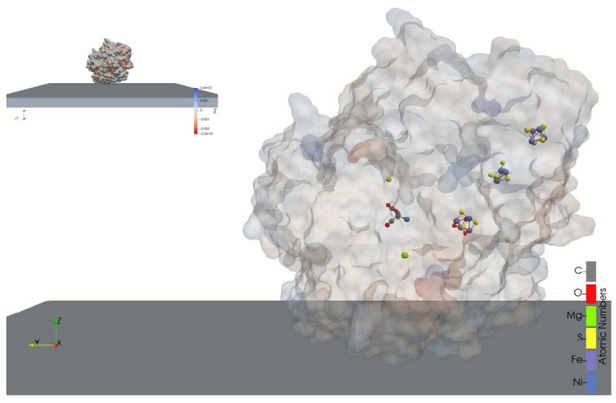


Figure 4. Representation of the position with the lowest total energy of the set of calculations done at pH 9 and 0.05 V. Under these conditions, the external FeS cluster was placed far to the surface of the electrode, flipping up the protein. The resulting position could interrupt the flux of electrons and the production of hydrogen.

Two of the most representative results obtained are shown in this poster, the total energy values are represented as heatmap plots (figures 1 and 3), while the most probable orientation at pH 6 and 9 are presented in figures 2 and 4.

5. Conclusions

The orientation of the hydrogenase can be manipulated modifying the pH, and the electric potential applied to the electrode. At the moment the preliminary results suggest that the best oriented positions are obtained at pH 6, positioning the external iron-sulfur cluster oriented towards the surface of the electrode, reducing the distance that electrons have to travel to the inside of the enzyme.

6. References and acknowledgements

1. Bat-Erdene J., Welch J., Kondo-Francois A., and Marquis C. 2013. Fundamentals and electrochemical applications of [Ni–Fe]-uptake hydrogenases. RSC Advances (3) 8142- 8159.
2. Cooper C. and Barba L. 2016. Poisson–Boltzmann model for protein–surface electrostatic interactions and grid-convergence study using the PyGBe code. Computer Physics Communications 202, 23–32.
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