Introduction to Fuel Cells

Anode (oxidation—loss of electrons):
\[ 2H_2 \rightarrow 4H^+ + 4e^- \]

Cathode (reduction—gain of electrons)
\[ O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \]

Overall reaction (redox):
\[ 2H_2 + O_2 \rightarrow 2H_2O \]

We will particularly interested in the oxygen reduction reaction (ORR) in this class
\[ O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \]
Explore mechanisms: ORR toy example

Overall Fuel Cell Reaction

\[ 2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O} \]

The steps highlighted in blue tend to be rate limiting steps in ORR
Volcano Plot

Previous research shows that binding energies of reaction intermediates are good predictors of catalytic activity.

How can volcano plots be explained?

Sabatier Principles

Interaction between a substrate and a catalyst needs to be “just right.” Too strong of binding means you can not remove the substrate from the material. Too weak means it is difficult to bind the substrate to the material.

Binding Energies

• Binding energy: energy required to separate a system into two parts

\[
E_{\text{binding-oxygen}} = \text{ } - + 0.5
\]

• In our case, the two parts will be the material and the adsorbent.

• The reference of the adsorbent will always be the stable form of the species

• \( \frac{1}{2}O_2 + M \rightarrow MO \) – What is the energy change in the chemical reaction?
Binding Energies

• What does a positive binding energy mean?
  – It is energetically unfavorable for the substrate to bind to the material
Explore mechanisms: ORR toy example

Overall Fuel Cell Reaction
\[ 2H_2 + O_2 \rightarrow 2H_2O \]

It will be difficult to get oxygen to bind to the catalyst!
Binding Energies

• What does a positive binding energy mean?
  – It is energetically unfavorable for the substrate to bind to the material

• What does a negative binding energy mean?
  – It is energetically favorable for the substrate to bind to the material
Explore mechanisms: ORR toy example

Overall Fuel Cell Reaction
\[ 2 \text{H}_2 + \text{O}_2 \rightarrow 2 \text{H}_2\text{O} \]

It will be difficult to remove oxygen from the catalyst!
Cohesive Energies

- Cohesive Energy: Energy difference between the energy of a nanoparticle or solid with the energy of the individual atoms not interacting (free atoms)

\[ E_{\text{cohesive}} = \text{energy of nanoparticle or solid} - \text{energy of individual atoms not interacting} \]

- Another way to think about cohesive energy is how much energy are you gaining from creating a molecular structure

- You can also think of it as a measure of stability
Cohesive Energies

• Cohesive Energy: Energy difference between the energy of a nanoparticle or solid with the energy of the individual atoms not interacting (free atoms)

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*where N is the number of atoms in the nanoparticle*

• Another way to think about cohesive energy is how much energy are you gaining from creating a molecular structure

• You can also think of it as a measure of stability
Cohesive Energies

• Let’s say I want to compare the stability of a 38 atom and a 55 atom nanoparticle using the equation given. Can I directly compare cohesive energies? – get a per atom cohesive energy

\[ E_{\text{cohesive}} = \text{number of atoms} - N \]

where \( N \) is the number of atoms in the nanoparticle
Units

• We will be using the following units in this class:
  – Energy ➔ Electronvolts (eV)
    • The energy in one photon of visible light is 1.6-3.4 eV
    • The energy to break a covalent bond in Silicon is around 1.1eV.
    • Energies on an order of magnitude higher than this are too high!
  – Length ➔ Angstrom (Å)
    • The bond lengths are typically around 1-3 Å
Overview of VASP command line tools
Required calculations

When calculating binding and cohesive energies, you will need to *locally optimize or perform a geometry optimization* of each structure involved.

\[ E_{\text{binding-oxygen}} = \text{Material + Oxygen} - \text{Material} + 0.5 \]

For an oxygen binding energy on material, M, you will need to perform three geometry optimizations– M-O, M and O\(_2\).

You will need to check that each optimization successfully converges (\(|\text{\(F\)}}| < 0.005\text{eV/Å}\)). Next I will show you the tools required to check this with VASP.
Geometry Optimization with VASP

• You will use a software package called VASP to run these calculations; this software uses *Density Functional Theory (our electronic structure method)* to calculate properties of materials.

• These calculations will be much slower than your previous lab; the will take several minutes to run or even longer if all of the computer is being used!

• Next I will show you the tools required to check this with VASP.
## Command line for VASP

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<th>Force Type</th>
<th>RMS Value</th>
<th>Threshold</th>
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<td>1.492597</td>
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*Make sure this force value reaches threshold (<0.005 eV/Å); This parameter is specified in the INCAR file with the flag EDIFFG.*
## Command line for VASP

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Review: Algorithm for local optimization while using an electronic structure method

The general procedure for numerical geometry optimization is as follows:

1. Calculate the force on all atoms for some configuration of an atomic system.
   
   1. To calculate the force on all the atoms (fixed nuclei fixed) we will need to optimize the wave function for all the electrons in your chemical system

2. If the magnitude of the force is less than threshold, you have found a critical point! STOP.

3. If not, move the atoms, or *nuclei*, such that they go towards a critical points

4. Repeat.
Command line for VASP

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<th>Optimization step number for the electrons at fixed nuclei</th>
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More VASP Info

• What does the script vfin.pl do?
  – Moves all VASP output files to a directory you specify
    • e.g vfin.pl min1 places these files in directory min1
  – It leaves all starting VASP files (POSCAR, INCAR,POTCAR,KPOINTS,frilab.sub) in your current directory
  – The **POSCAR** file in you current directory, the new starting configuration, becomes the final configuration from the previous run or the **CONTCAR** file

The **XDATCAR** is a movie of all images in the optimization
Common Issues on Lab 2

• Calculations are not converged

Make sure this force value reaches threshold (<0.005 eV)

If not converged “wrap up” calculation and run the job again by running `vfin.pl minX then qsub frilab2.sub`