A graph of activity and activity

Description automatically generated

Figure 17 - The estimated activities based on two different calculations. Using all COOH binding energies (blue) and using only the COOH binding energies from on-top sites, which does not have a neighbouring hollow site, where H has a negative binding energy. These sites are assumed to be CO-poisoned due to the COOH+H disproportionation reaction, and are counted as a 0 in the activity sum.

A chart of content

Description automatically generated

Figure 19 – Ternary activity plot with 5% molar fractions of platinum, silver and gold. The highest activity found was 5.2\*10e-6 at the composition Pt0.8Ag0.2 at the potential (eU) of 0.07 V vs RHE.

In figure 17, the metals platinum, silver and gold has been chosen, with all 5% molar fractions

A pyramid of content

Description automatically generated with medium confidence

Figure 20 - figure

Fedt

A pyramid of content

Description automatically generated with medium confidence

Figure 21 - Ternary activity plot based on 5% molar fractions of palladium, gold, and silver. The optimal composition when restricted to the three selected metals is Pd0.9Au0.1 with a comparably low activity of 2.4\*10e-10 at a potential (eU) of 0.2 V vs RHE.

Tekst

**DFT calculations**

***Slabs for testing CO-OH slide reaction***

what was the conclusion on this? Seemed unreasonable?

I guess basically the story is: FA has a high theoretical efficiency, but is plagued by very low activity until the voltage has been increased to clean the surface, pointing towards a

Single-site anode catalysts have had success (refx3), so this points towards a hypothesis that is xx, hence it should be investigated how and why and if it can be replicated theoretically and computationally to learn more about it and perhaps peep into optimizations.

***Bayesian optimization***

Math explanation, practical – Explain in introduction or methods?

In figure x, two activity estimation routines are compared on varying potentials (eU) for the same simulated HEA surface. The simplest routine, shown in blue, involves just applying equation x to all binding energies of COOH on on-top sites of the simulated surface. This activity increases as the potential (eU) decreases from 0.2 V and achieves the maximum activity at the optimal potential calculated to -0.17 V. However, formic acid oxidation is assumed to be held back by CO oxidation, so the activity estimation function needs to account for that in order to accurately predict FAOR performance. This routine is shown in orange, and as expected shows an increasing activity when the potential decreases from 0.2 V, but then is decreases by hydrogen UPD, which starts poisoning on-top sites around 0.1 V and has poisoned every site around 0.16 V. A maximum is found in the middle, typically between at small positive potentials around 0.07 V, depending on the surfaces ability to deter H adsorbing to neighbouring on-top sites. A theoretical surface with large positive binding energies for H in hollow sites and low COOH binding energies on on-top sites would be able to be most active at a lower potential, which would improve the efficiency.

A brute-force search approach has been used on the stoichiometries / molar fractions to find the most active composition of the surface. Molar fractions of 5% intervals was made for all five metals, leading to 10626 compositions, and from each composition a 200 by 200 by 3 surface was simulated, the binding energies of COOH and H predicted by the appropriate model and the activity estimated.

Based on the COOH binding energies as shown in figure 8, it’s known that either platinum or palladium is needed for formic acid oxidation, but pure platinum or palladium surfaces might not be optimal anode catalysts due to CO poisoning. Hence, examining the impact of silver, gold, and copper along with platinum and/or palladium on the formic acid oxidation activity is of interest.

When testing all 5% molar fraction the highest activity is found at this stoichiometry at this potential.

With ternary activity plots, plotting the activity of all possible molar fractions of a trimetal is possible.

The hunt is therefore on for an atom on the periodic table, which fulfils the criteria for an optimal catalyst.

Scaling relations might be a hindrance

COOH needs to bind way stronger, but that is correlated with a stronger H binding in general. Can this be circumvented with single-sites or will H just move on-top and block?

The optimal anode potential sets some pretty rough criteria. Also, the activity increases at higher potentials and the efficiency per HCOOH increases with the open-circuit voltage as

De forskellige potentialer vs RHE

CO oxidation and CO creation.

Note: Nifty that I have neighbour DFT data that might be able to show the same thing.

Note: Go into specifics with different reaction pathways? Mention the dentates? Or just show the free energy diagram later and say it doesn’t look feasible? Based on DFT data the energy increases.

Show free energy diagrams – optimal binding energy and perhaps one with voltage that makes them equal in energy? And one with the energies from

Måske vis, at man kan bruge Pt som reference, og så notere bindingsenergier som “den binder så godt her ift. Platin”, og det har man for OH og det dobbelte for O, men der er ikke for COOH og dentaterne. (Eller ligegyldigt måske? Jeg burger det jo ikke)

Kohn-Sham DFT applied to calculate the binding energies of various adsorbates.

Hohenberg-Kohn proved, that electron densities can perfectly describe a quantum system. Two theorems. 1: Unique one-to-one mapping between ground state energy of system and its electron density. 2: A variational principle holds for electron densities; the electron density can be found by minimizing the expectation value of the energy (Jacks sætning) (Det hele skal omskrives en gang ekstra, selvom intet er kopieret direkte)

**Plotting GH vs GCOOH**

Plotting them H vs COOH

Using energy prediction models on simulated surfaces

The optimal achievable U\_anode might be found in the region just above the potentials, where both H and COOH is present, even though lower COOH binding energies would be more efficient in terms

Then, the challenge of finding the optimal

Describe the criteria used to judge stochs through their binding energies

Swim ring combinations binding energy plots

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Fuel | Gravimetric energy density (kWh/kg) | Volumetric energy density (kWh/L) | Max theoretical efficiency | Reaction steps | Price (US$/kg, retail) | Operating temperature (°C) | Storage vessel | Storage pressure |
| FA |  |  |  |  |  |  |  |  |
| H2 |  |  |  |  |  |  |  |  |
| CH3OH |  |  |  |  |  |  |  |  |

The electrical energy released by FAOR per electron can be estimated with the free-energy diagram of the direct pathway, as seen in figure x.

FOAR highest U vs CHE: negative

OER highest U vs CHE: positive

The difference is the V\_OC

#If formate binds too weakly, the potential can’t be lowered much, before the binding reaction is no longer favourable, leading to a small open-circuit voltage. If formate binds too strongly, what happens? (Tjek ask Jack).

**Notes for formic acid:**

Already close to CO2 in structure, compare to other species like methanol, ethanol. More effective with fever electron transfers and steps. Plot similar to the one from Jack with energy efficiencies

Methanol has a CO base, while formic acid has a OCO base. Methanol has 4 H. So the methanol oxidation requires a pretty large overpotential, which FAOR doesn’t need. This means the potential optimal decent working potential is lower for FAOR.

# How much energy comes out? Per electron? To calculate the maximum electrical energy

Make a simple figure that shows both methanol and formic acid with the backbone highlighted.

Kilder til HEA:

1. [15]  Z. Y. Lv, X. J. Liu, B. Jia, H. Wang, Y. Wu, and Z. P. Lu. Development of a novel high-entropy alloy with eminent efficiency of degrading azo dye solutions. Scientific Reports, 6(34213), 2016. https://doi.org/10.1038/ srep34213.
2. [16]  Chih-Fang Tsai, Pu-Wei Wu, Pang Lin, Cheun-Guang Chao, and Kung-Yu Yeh. Sputter Deposition of Multi-Element Nanoparticles as Electrocatalysts for Methanol Oxidation. Japanese Journal of Applied Physics, 47(7R):5755, 2008. https://doi.org/10.1143/JJAP.47.5755.

Her er Kohn-Sham-Hohenberg-referencerne:

1. [20]  P. Hohenberg and W. Kohn. Inhomogeneous electron gas. Physical Review, 136(3B):B864–B871, 1964. https://doi.org/10.1103/PhysRev.136.B864.
2. [21]  W. Kohn and L. J. Sham. Self-consistent equations including exchange and correlation effects. Physical Review, 140(4A):A1133–A1138, 1965. https: //doi.org/10.1103/PhysRev.140.A1133.

Estimating the energy barrier of something with some other number

***Overpotentials (Prob done already elsewhere)***

***Cyclic voltammetry***

***Polarization testing***

How are experiments made in electrocatalysis? Polarization testing. Talk about a few experiments, perhaps here mention the CO problem and say “so nice, that I made neighbour DFT data”. Setting voltage manually just on the anode catalyst to see what sits on the surface. Controlling the current, and noting the voltage?

Show U = R \* I ? xD And P = U \* I

Tuning the fractions (Gjort I Jacks ref 3 på en specific reaktion) in general could fit any reaction, in this work applied to formic acid oxidation.

\*poisoning effect and Perturbations\*

In this work a “forbredning” of the predicted binding energies is seen when simulating surfaces

(ref: Jack kilde 15 og 16 til brug af HEA I experimenter)

Some differences due to blocking and coverage effects making the last

Achieving the exact optimal adsorption energy of a given species

This work seeks to optimize a reaction, in which the activity of the reaction pathways is dependent on specific requirements to the binding energies of different adsorbates.

*Motivation: Why are HEA’s interesting*

*High-Entropy Alloys (HEAs)*

*Class of materials 2004 paper*

*High configuration entropy*

*tune poisoning effect*

*Perturbations*

*Stability of HEAs* (Learn about it from Jacks thesis and google some more)

Mean-field approximation for coverage

Jack mean-field paper

All elements used have FCC structure

How and why and where do different adsorbates sit?

Show a fcc(111) surface and hollow, on-top, mixed site

presenting the adsorbates (Done in data figure)

Look at Jack’s thesis to perhaps sniff out the relevant topics/theory

***Heterogenous Catalysis***

Diagram: A and B, bonding, AB, reaction, etc.

Activation energy lowered

Arrhenius, reaction rate coupled with activation energy

Sabatier then has a contribution regarding binding energy, getting to the surface vs getting off (diffusion)

And then more complex part about specificity towards direct FAOR, which also depend on binding energies

Show the proof for the best mix: (Move to results?)

Coming up with an input that describes the situation adequately, that a model can fit to

Regression to a real numbered target

Treat dft as known targets. Try to get the regression model to predict DFT calculated binding energies

Small paragraph on machine learning in general. Regression/classification

Unknown function between a list of inputs and an output (structured ml problem)

Gradient-Boosted Decision Tree (GBDT)

How do decision trees work, simple example, some equations, etc. maybe a lil image. Ohh maybe the start of the actual tree from one of my best models:)

Regression

The calculations are based on the projector-augmented wave (PAW) method, where the wave functions are described with plane-waves. (Recap possibly not needed).

Notes:

. Looking at the

The single adsorbates of interest are shown in figure wholepageslabfig and are: H, COOH, CO, OH, O.

The neighbour-adsorbates of interest are: H + COOH, CO + OH

Make a table that shows what type of site they sit in? I gotta explain the site types first. And why they are stabilized at surfaces, besides just “energetically favourable”.s

A boring table with the number of sites, etc.?

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Adsorbate** | COOH | H | CO | OH | O | H+COOH |
| **Site-type** | On-top | Hollow | On-top | On-top | Hollow | Neighbour on-top and hollow |

Explain why these were made and what they are good for

Slabs for estimating H+COOH neighbor interactions

#Maybe I should have made CO+O (I have CO+OH slabs) lmao. To get a more accurate assessment of when O would adsorb next to it. But the most important thing is that CO doesn’t happen at all, so it’s not critical – move to future work haha

Mimics single-sites

Slabs for estimating swim ring efficiency

, because as seen in both pure metal slabs and HEA slabs, the sites with Pt and Pd bind COOH and H stronger than Cu, Au, Ag.

An example is the binding energy from the adsorption reaction of COOH from HCOOH:

With the binding energy elucidated from DFT calculations on slabs and single molecules:

Show the calculations here like the ones I drew in ppt: \*COOH minus \* minus COOH from dft as well

(In the plot by alexander these are shown)

. (Tjek: Så få nævnt ren Pt nu)

NOTE: add, that these borders are for even steven HEAs.

OH and O:

Show calculations, corrections – skal der nogen ekstra corrections med der?

Also Bagger article showed the activity of FAOR increasing significantly around

This would make sense with a potential around 0.25 eV

Thermal corrections for the relevant species have been estimated by Chan et. al., and gives the following correction constants:

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Species |  |  |  |  |  |
|  |  |  |  |  |  |

The correction constant for COOH

These correction constants (both based on CO2+H2 and HCOOH) predicts that COOH wouldn’t bind (Or only at high voltages? But then CO poisoning wouldn’t be a problem)

Corrections for COOH and H are similar to the ones used in A. Bagger article. They are based on calculated thermal corrections from the BEEF-vdw functional. The corrections should in theory be identical across functionals.

Put in formulas from the notes and explain

Basic adding and subtraction stuff – account for all atoms, leave the binding energy.

Transform from electric DFT energies to Gibbs free energies with Chan numbers.

Surface slabs -> Feature vectors -> Input

DFT calculations -> Binding energies -> Target

Træn indtil konvergens

Tjek: Kig lige på den store data-figur og få skrevet max 10-15 linjer om det her.

, and

General task

Surface to trainable parameters -> Features

Same adsorbate – Both HEA and SWR (SS) data combined. Separate test/val/train split

On-top

Hollow

Mixed-site (combined vector, subtract each adsorbate)

Given energies

and all the equations and figures of them would be nice

Lige nævn XGBoost en gang?

The optimal composition is the composition, that leads to best FAOR performance. The two most important measurable parameters are the overpotential (The open-circuit voltage maybe?) needed to make FAOR happen and the current

Tjek: what about activity? Explain the tradeoff between activity and open-curcuit voltage and hence, efficiency per molecule

Optimally, FAOR would happen as early as possible, at no overpotential, and have a large per-site current. Currently, the FAOR happens at an overpotential, due to surface sites not having the optimal binding energy for \*COOH. The per-site current is, in the literature (Kilde: Alexander and others), assumed to be

As seen in alexander, they needed to go to

Composition space

This project will

In the cases where the optimal compositions seems to be comprised of 3 elements,

How much can CO-poisoning be circumvented with tuned HEA on fcc(111) facet.

3 ele

Explain overpotential

Explain Efficiency per molecule formic acid.

The per-site activity of the two-step reaction (direct FAOR) is modeled with the equation:

because the aim of the work is to discover HEA catalysts that circumvent CO-poisoning and with the volcano method,

Only if the COOH binds even better than that will the reaction not be favoured and go uphill

Reaction window: COOH binding energies are allowed to be between 0 and -0.34 at = potential. CO2+H2 energi lowers with 2 eU, faster than COOH at 1eU.

Another possibility is using a sim

Two possibilities, using the activity estimation formula from OER and a simpler method counting the active non-poisoned sites.

We are interested in a descriptor that accounts for CO-poisoning clearly, and with the OER-based activity measure the potential makes a much bigger impact than the tuning of the surface, especially at low potentials.

The FAOR performance is based on the activity on the on-top sites.

The activity on an on-top site is assumed to be 0, if H is adsorbed onto a neighbouring hollow site, assuming that the disproportionation reaction producing CO takes place.

Then, one can choose between using the

The activity estimation has the following procedure, where the activity of each on-top site is estimated. (A potential is given? Or determined by the COOH binding energies?)

* Check if any of the neighbouring hollow sites would adsorb H
  + If they would, then the disproportionation reaction is assumed to produce CO and block the site. Activity is set to 0
  + If not, proceed:
* Evaluate the activity based on the COOH binding energy

**NEW Counting activity measure**

So that was interesting, but that activity measure was made for ORR? And has some assumptions, which we don’t even know if they apply to FAOR.

Therefore, we employ a simpler activity estimate based on a count of binding COOH, not discriminating based on the exact binding energy, just the fact that it binds. FAOR is then assumed to happen when COOH binds in the first place.

Using a simpler counting activity measure:

Assume each bound COOH reacts and disqualify it, if neighbouring H bind. Count the number at each potential and see how far you can get down without losing activity.

Would this assumption fit the Bagger results better?

Test all molar fraction mixes with both activity estimates and test all the funky single-site surfaces.

Show the number of available sites as a function of potential. Can Single-site structures

that leads to optimal activity

of pair energies

Show how to estimate the per-site current. Ref to the free-energy diagram of the direct FAOR pathway.

Optimization (different optimization criteria both single and given)

**Simulating surfaces – should be in methods?**

Initially, the models are used on a high entropy alloy with an even split between the five chosen metals.

**Coverage simulations**

A coverage simulation is a simulation, that tries to mimic the behaviour expected in electrochemical experiments during a potential sweep as seen in cyclic voltammetry. The simulation utilizes simulated surfaces and binding energy prediction models trained on DFT. The routine is implemented in the following general steps:

Set initial parameters: Surface dimensions, voltage range, voltage step size. Steady-state is assumed at each voltage step.

Simulate a custom surface, for example a standard HEA surface or a surface designed with single-sites. The surfaces have the dimensions 3x200x200. Before the potential sweep, the binding energies for all adsorbates on all sites are predicted and the voltage at which the adsorbates would be energetically favoured to desorb or adsorb, labelled the “border voltage”. Depending on the adsorbate’s adsorption reaction, it either adsorbs over or under its “border voltage”. If the proton-electron pairs are on the left side of the adsorption, the reaction is encouraged by a low potential and vice versa.

At each voltage in the potential sweep, the following steps are done:

1: Look at each site on the surface

2: Identify if there is an adsorbate on the site. If there is, check its “border voltage” to determine if the adsorbate should desorb or remain. If there is no adsorbate, check if any of the possible adsorbates have a negative binding energy as seen in their “border voltage”. Each time a reaction happens (adsorption, disproportionation, oxidation) a line with details is written to a log file.

3: Reactions between neighbouring adsorbates take place. The surface is scanned for H+COOH neighbour pairs and CO+OH or CO+O pairs for oxidation of CO.

Plot info box that shows the outline of the algorithm/routine?

Plot an example of a coverage simulation – Maybe a surface where a decision is being made and a voltage is given. Show all the stats, binding energy, border voltage, and decision.

**Reactions**

Show the disproportionation reaction and the oxidation reactions.

Show how the border voltages are calculated here.

Tjek: Mention the extra corrections in the plain text in chan et al.

Tjek: Move calcs up here? Don’t make the specific calculations here, have them in methods. Make this section just theoretical

Tjek nævn Beef-vdw korrektionen?

and this requires information on the local environment from both adsorbates. T

55-length vectors

20-length vectors,

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Central atom | Pt | | | Pd | | |
| Surrounding atoms | Cu | Ag | Au | Cu | Ag | Au |
| Activity | 2.7\*10e-5 | 4.3\*10e-6 | 4.2\*10e-6 | 7.3\*10e-12 | 1.5\*10e-11 | 3.9\*10e-14 |
| Potential at max j (eU) [V] | 0.02 | 0.08 | 0.07 | 0.09 | 0.06 | -0.02 |

# Corrections for OH and O:

Chan et. al approximates a solvation effect of -0.5 eV for , which is included in the thermal corrections for and marked with bold in the calculation. The thermal corrections for are based on their adsorption reactions and adsorption energies:

The thermal correction from electronic DFT energies to Gibbs free energies for is then:

The thermal corrections for are based on their adsorption reactions and adsorption energies:

The thermal correction from electronic DFT energies to Gibbs free energies for is then:

|  |  |  |  |
| --- | --- | --- | --- |
| Species/Thermal | ZPE | CpdT | TS |
|  | 0.62 | 0.10 | 0.19 |
|  | 0.28 | 0.09 | 0.40 |
|  | 0.90 | 0.11 | 0.99 |
|  | 0.23 | 0.01 | 0.01 |
|  | 0.57 | 0.10 | 0.67 |
|  | 0.36 | 0.05 | 0.08 |
|  | 0.07 | 0.03 | 0.04 |



Figure 12 - Some text

The MAE of the on-top OH model is 0.039 eV, and the hollow-site O model is 0.056 eV and the loss curves show that the validation loss is very close to the training loss, which shows good learning. These five models, and their predicted electronic binding energies will be the basis of the further applications.

They show, that on an equimolar fraction HEA surface, OH and O starts adsorbing at an anode potential of 0.xx V vs RHE, at which point any CO-poisoning would start to be oxidated and removed. At that potential, the open-circuit fuel cell potential is 0.xx, which is very inefficient. Thanks to the models, we now know, that it is crazy bad to have to go to that high potentials to clean the surface. TJEK

# TO SI: