Abstract

**Introduction**

**Climate change (**Causes, effects, history, societal challenges, numbers, IPCC reports**)**

***History***

In 1896 Svante Arrhenius published a paper, where the link between CO2 and the temperature of the ground is made for the first time (kilde til S. Arrh). In 1939 Guy Callendar argued, that anthropogenic emissions of CO2 had raised the CO2 content in the atmosphere by 10 percent since 1900 (kilde til Nasa artikel), while others (Roger Revelle) believed, that the biosphere would have absorbed the anthropogenic emissions. In the 1950s a group of oceanographers and geochemists were concerned with the CO2 concentration of the atmosphere because the ocean absorbs CO2, leading to more acidic surface water, which would affect sea life (kilde til Nasa artikel). In 1957 Charles David Keeling was hired at a postdoctoral scientist position by Roger Revelle and ordered to measure the CO2 concentration in the atmosphere at Mauna Loa, Hawaii. The CO2 concentration was measured with an infrared gas analyzer, that determines the absorption of an infrared light source through the surrounding atmosphere. Different atmospheric gasses absorb at different wavelengths, hence the adsorption at specific wavelengths can be related to atmospheric content of various gasses. (Basic, ingen kilde?)

The results of Keeling’s measurements were clear, the CO2 concentrations rose even during the short 18-month period of measurements. The measurements suggested that at most half of the anthropogenic CO2 emissions had been adsorbed by the biosphere. The plot showing CO2 concentration in parts per million as a function time was coined the Keeling curve and has been measured since, showing the increase in CO2 ppm rising from 313 ppm on March 29, 1958 to 421 ppm on august 2, 2023 (Kilde: Keeling Curve, ACS). Historical data on CO2 concentration in the atmosphere can be estimated before direct measurements were made via ice cores drilled up in Greenland and Antarctica. The past 800.000 years’ atmospheric content is trapped in the ice that froze each year and can be analyzed now, giving a long-term historical perspective and data used to model climate change (Kilde: Ice cores).

PLOT: Keeling curve?

***Causes***

The core mechanism behind climate change is based on the interaction between infrared and visible light and so called “Greenhouse gasses” (GHGs). Electromagnetic radiation from the sun enters the atmosphere and reaches earth’s surface, where some of it is adsorbed, heating the surface, and some is reflected, possibly leaving the atmosphere again. The heated surface in turn reradiates some of the energy as infrared radiation, as described by Planck’s radiation law. GHGs interact with the infrared radiation to adsorb and re-emit infrared radiation in all directions, about half back onto the earth’s surface. This mechanism allows energy from sunlight to pass through the earth’s atmosphere unobstructed by the GHGs, while returning half of the energy from reemitted infrared radiation from the surface, creating the “greenhouse effect” (Kilde: Greenhouse\_effect).

The carbon cycle consists of large amounts (gigatons) of CO2 being recycled through emitters like microbial respiration and decomposition and plant respiration and adsorbers, mainly photosynthesis. The anthropogenic carbon emissions offsets the balance between these, resulting in an atmospheric carbon net annual increase. The anthropogenic carbon emissions stem mainly, 91 % in 2022, from the combustion of fossil fuels, such as oil, coal and gas (kilde: GlobalCarbonBudgets). An example of a combustion reaction of a fossil fuel is the aliphatic hydrocarbon C10H22, present in diesel fuel:

An alternative to fossil fuels is renewable energy, which harnesses the energy from renewable resources such as solar, wind, hydropower and geothermal. These renewable energy sources do not emit CO2 when producing energy, contrary to fossil fuels which, in the case of oil, returns carbon in the form of hydrocarbons from underground reservoirs back to the atmosphere.

***Effects***

The direct effects of the anthropogenic GHG emissions are plentiful and a “threat to human wellbeing and health of the planet” (Kilde: IPCC feb 28). The average temperature of the atmosphere increases and has increased around 1.1 degrees Celsius since 1880 (Kilde: Earth observatory Nasa), projected to make 20 % of the planet a “barely livable” zone purely because of the heat (Kilde: IPCC). The oceans are getting warmer and more acidic, due to the ocean absorbing 20 to 30 percent of all anthropogenic CO2,emissions posing a threat to ecosystems that inhabit the oceans (Kilde: Earth obs Nasa). Ice sheets on Greenland and Antarctica have declined in mass, leading to increasing sea levels, that threaten to flood the homes of 300 million people (Kilde: New elevation data). Furthermore, the frequency of extreme weather events is increasing (Kilde: CSSR ’17). From all this, it is apparent, that climate change is an issue on an apocalyptic scale, that must be addressed in order to secure human wellbeing and long-term existence on earth.

The production of primary energy on earth increases steadily, as developing countries advance infrastructurally and technologically, highlighting the need for renewable and sustainable energy sources to replace fossil fuels. This calls for development of technology that can aid the transition to renewable energy sources. To shift all carbon emitting processes to renewable, non-carbon emitting sources of energy would require many different solutions, both in terms of energy storage and fuel cells. Container ships, cars, and airplanes, three large fossil fuel reliant transport vessels and carbon emitters, have very different needs in terms of capacity, weight limitations and power consumption. The electrical grid would also need to have a large-scale battery in order to supply electricity produced from renewable sources at all times, even when wind and solar do not produce energy and fossil fuels take over. One solution to storing energy from renewable sources is green fuels and fuel cells. Bearing in mind that 91 % of all anthropogenic emissions stem from energy production with fossil fuels, a complete transition of the energy sector to provide plenty of renewable energy, both to developed and developing countries with growing energy needs, is essential to tackling climate change (Kilde: GlobalCarbonBudget).

**Fuel Cells**

A fuel cell is an electrochemical cell that converts the stored chemical energy in the fuel into electricity through a series of chemical reactions, rather than a combustion. The “green” fuels for fuel cells are made with electrochemical reactions using surplus renewable energy. The fuels then serve as an alternative way to store excess electrical energy compared to conventional electrical batteries. Storing excess electrical energy as green fuels has a variety of advantages. The storage space for a liquid green fuel is cheaper than a Li-Ion battery with the same energy capacity and can be stored for long periods of time without self-discharging and cycle indefinitely without decreasing the max capacity, as Li-ion batteries do when degrading. Furthermore, Li-ion batteries suffer from low gravimetric and volumetric energy densities. A drawback of green fuel and fuel cells is the round-trip efficiencies, where lithium-ion batteries generally have round-trip efficiencies (RTEs) of 90%+, while hydrogen has an RTE from electrical energy back to electrical energy of 18-46 % (Kilde: Flora, Nature Energy). Worthwhile green fuel production hence requires both an efficient oxidation reaction of the green fuel and an efficient reduction reaction of the precursor to the fuel. Efficient round-trip efficiencies are therefore highly reliant on the development of tailor-made catalysts for these reactions.

***Structure***

A proton-exchange membrane (PEM) fuel cell consists of two separate inlets for fuel and O2 atfuel field plates, a gas diffusion cathode and a gas diffusion anode, a catalyst layer at each electrode and a PEM to separate the electrodes (Kilde: ?). The PEM is an electrically insulating layer, that allows the passage of protons. The catalysts at each electrode should ideally bind the intermediates of each half-cell reaction at the optimal binding energy, in order to reduce the overpotential. The green fuel enters the inlet at the gas diffusion anode, where it partakes in the oxidation half-cell reaction. When the fuel has been oxidized, the excess proton-electron pairs (H+ + e-) split up, as the proton moves through the PEM to the cathode, where it will partake in the reduction half-cell reaction, where an electron will then be needed. This creates a voltage difference between the negatively charged anode and the positively charged cathode, from which an electrical current can be pulled. An assembled stack of PEMs constitutes a Membrane Electrode Assembly (MEA). In the case of direct formic acid fuel cells (DFAFCs), there are three main ways of supplying the fuel. Active DFAFCs, where fuel and oxygen in compressed air are delivered to the inlets vie pumps, active air-breathing DFAFCs, where fuel is pumped in, but the oxygen is supplied from exposing the cathode to the ambient air, and passive air-breathing DFAFCs, where both fuel and oxygen is supplied by diffusion from a fuel tank and ambient air (Kilde: from CO2 to). A DFAFC PEM fuel cell has a theoretical open-circuit voltage of 1.48 V, which is promising in terms of fuel cells, but low compared to car and truck batteries at 12 or 24 V (Kilde: CO2 to FA). Fuel cells are therefore connected in series to increase the net voltage or in parallel to increase the current, both resulting in a higher total power output, which needs to be 112 kW to supply 150 Horsepower for an average family car.

***Reactions***

Fuel cells harness the chemical energy stored in the green fuel molecules with a set of redox-reactions, namely two half-cell reactions. In the oxidation reaction, the fuel is reduced a number of times, each producing a proton-electron pair. In the reduction reaction a molecule, typically O2, is reduced to H2O. The simplest example is the half-cell reactions in a hydrogen fuel cell, that has the oxidation reaction:

And the 4e- pathway of the oxygen reduction reaction (ORR):

Resulting in a total reaction of hydrogen reduction:

Formic acid (FA) can be reduced to CO2, providing two electrons, as seen in the half-cell reactions. The oxidation reaction is a two-step reaction, where each step releases a proton-electron pair:

The reduction reactions are the same as for the hydrogen fuel cell, with gaseous oxygen being reduced to water:

Resulting in a total reaction of formic acid reduction:

Methanol, a direct competitor to FA, provides 6 proton-electron pairs per reacted molecule, compared to 2 for FA, resulting in an around 3 times higher volumetric energy density. That also leads to a more complicated oxidation reaction, that involves six reaction steps instead of the two for FA (Kilde: Fundamentals)

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| 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 | (Kilde til en del af det: CO2-artiklen) |  | Make sure to mention this chart in the text |  |  |  |  |  |
| H2 |  | Maybe not |  |  | Worth filling | In in word | If I have to | Hand in |
| CH3OH |  | In LaTeX anyways |  |  |  |  |  |  |

In the chart xxx a comparison (Kilde: CO2)

Show the chart from Jacks thesis and cite him

***Formic acid***

Formic acid (FA) is a promising green fuel, primarily because of its high volumetric energy density (2.13 kWh/L), open-circuit voltage (1.48 V) and theoretical energy efficiency (58 %) (Kilde: Eppinger). Formic acid is a liquid at standard conditions and an acid with a pKa of 3.7 and it is non-toxic and present in small quantities in foods and vegetables. Formic acid is therefore safe and easy to handle, as opposed to methanol, which is toxic. Formic acid being a liquid means it doesn’t have to be pressurized, as opposed to hydrogen, which makes storage easier and cheaper and contributes to its high volumetric energy density.

FA can be used as an energy carrier for fuel cells with CO2 as “carbon feedstock” (Kilde: CO2). FA is an obvious choice for a cycle with CO2, since they are reasonably similar in structure, the only difference being two hydrogen bonds on C and O. This makes electroreduction and oxidation somewhat simple, as a middle ground between H2 and CH3OH. The production of FA with electroreduction of atmospheric CO2 as the starting compound and the oxidation of FA in a fuel cell represents a closed carbon loop capable of storing energy from preferably renewable electricity sources. When FA is produced by electroreduction of CO2, cell conditions are neutral to alkaline and produce formate (COOH-), which becomes FA when the pH is lowered (Kilde: CO2).

Formic acid has a direct oxidation reaction (FAOR) pathway from FA to CO2, where the two hydrogens separating CO2 and FA is removed one at a time with bound COOH as an intermediate and an indirect pathway where CO is formed as an intermediate, which requires a large overpotential to oxidate to CO2. CO oxidation requires bound O or bound OH to form on the surface on a neighbouring site to CO, which then participate in an oxidation reaction. Making an efficient catalyst for formic acid therefore requires a high specificity towards the direct pathway, that discourages CO from forming. If an overpotential is not applied to oxidate and remove bound CO from the anode catalyst surface, many sites will be blocked, reducing maximum current greatly, as shown experimentally (Kilde: Alexanders f.eks.). In the literature, a handful of possible FAOR pathways are suggested, but the primary two pathways assumed to be important are the direct (HCOOH -> \*COOH -> CO2) and the CO-producing (HCOOH -> \*COOH -> \*CO -> CO2) (Kilde: Alexander og andre):  
Note: Show the CO-producing reaction pathway here.

Talk about the sites where \*COOH and \*H sit as neighbours and that single-site anode catalysts have been tested showing good results, indicating that the assumption about CO-poisoning might be right. (Kilde: single-site experiments). Note: Nifty that I have neighbour DFT data that might be able to show the same thing.

**Notes for formic acid:**

Formic acid oxidation (FAOR) is currently assumed to be held back by CO-poisoning, leading to experiments

Note: Go into specifics with different reaction pathways? As shown in Alexanders article

Show the specific reactions with nice illustrations (The ones from powerpoint perhaps, or just Alexanders)

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

Chemical storage of energy, that contrary to fossil fuels can be electrochemically returned to its low-energy state without combustion or a net production of CO2.

Notes: Difference between combustion and electrochemical reaction

Chemical energy in both

Combustion loses a lot of energy to entropy.

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

Show the different adsorbates we’re working with

To calculate the maximum electrical energy

# How much energy comes out? Per electron?

**Catalysis**

Opening new pathways

The classic figure of the reaction diagram with an intermediate, lowering the barrier

***Modelling the activity of a site***

Free energy diagrams

Modelling the activity of the two-step reaction

Estimating the energy barrier of something with some other number

***Overpotentials***

***Sabatier’s principle***

***Cyclic voltammetry***

**Density Functional Theory**

DFT machinery

***Theoretical background***

***Practical use in catalysis***

**High-Entropy Alloys**

(Hvorfor – tune poisoning effect) motivation

Tune binding energies

Poisoning effect

How and why and where do different adsorbates sit?

***Single sites / Swim rings***

Single site anode catalysts have been tried with success (ref). The structure of a single-site is a metal A surrounded by metals B. Metal A is a metal that binds H and COOH relatively strongly like platinum or palladium and metal B is a metal that binds less strongly like Au or Ag.

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

The presence of single-site catalysts has been shown to work well for FAOR, hence achieving the highest possible occurrence of single-sites is of interest. Arranging the atoms on the surface in a specific pattern is not possible in a HEA, the only parameters are the stoichiometries of the metal alloy (for example Pt0.5Au0.5).

The problem is:

A surface composition is given as AaBb with f(A) = a and f(B) = b indicating the stoichiometry of each metal. The stoichiometries sum to unity. A single-site it defined as a motif where an A metal is surrounded by six B metals on an fcc(111) surface. The atoms are assumed to be distributed randomly on the hexagonal closest packed top layer of the fcc(111) surface. Which stoichiometry will lead to the statistically highest random occurrence of single-sites?

The odds of finding an A metal at a specific position is f(A), and the odds of finding a B metal on a neighbouring site is f(B) or 1 – f(B). The odds of finding six neighbouring B metals independently are then (1 - f(B))6. The odds of finding a single-site (ss) are then:

Increasing the contents of A increases the odds of finding A metals that could possibly be a single-site, but at the same decreases the odds of finding six B metals surrounding it. To find the equilibrium f(A) that maximizes f(ss) the function is afledt ift f(A) and set equal to zero, and isolating f(A), finding a top-point

The maximum per-atom odds of finding a ss is:

When including two B metals, that bind H and COOH weakly, they can share the fraction amongst them, eg. .

The results have been verified by a simulation, as shown in figure x (insert plot). In the simulation, a 1000 by 1000 top layer of a surface have been created with a range of 1000 evenly spaced f(A) values between 0 and 1. The number of ss are found by scanning each site on each surface. (Tjek - Potentially show the optimal surfaces)

**Machine Learning**

Small paragraph on machine learning in general. Regression/classification

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

In our case DFT data is expensive, so we only make a limited amount of “gold” labels with DFT and use a regression model to extrapolate to arbitrary sites. Because of the complexity of the sites, with the number of metals and atom positions in the surface that has a contribution to the binding energy (Ref the article that claims to estimate about which atom positions are relevant). The quality and accuracy of the model can be verified and estimated by splitting up the total dataset into a training set, which is the only datapoints the model is “fitted” to, and a validation set used under training to ensure the model isn’t overfitted, and a test set, which the model tries to predict after training. The result on the test set is the best estimate of the accuracy of the model. More precise estimates on the accuracy of the model can be achieved by including a larger portion of the total dataset in the test set, but this also reduces the entropy in the training set, which means the model has seen fewer datapoints and will have a diminished predictive power. Ideally the model will have seen datapoints from every point in the catalyst composition space, but this is unfortunately unattainable due to computing times of DFT data points.

**Methods**

**Data**

***Technical details***

The Density-Functional Theory (DFT) calculations are carried out with the GPAW python implementation from (kilde). The calculations are based on the projector-augmented wave (PAW) method, where the wave functions are described with plane-waves. (Tjek more details)

The purpose of the DFT calculations is to evaluate the binding energy of the relevant species in FAOR. A range of slabs are made with different metal compositions and the slabs are saved with and without the specific adsorbate. In order to isolate the energy from the adsorption, the energy from the slab and adsorbate, the pure slab, and the molecule isolated is necessary. The energy calculations must be performed with the same functional to eliminate differences between different DFT implementations. The DFT routine calculates forces on each atom and moves them iteratively until the forces are below 0.1 eV/Å, and the electronic energy of the relaxed structure is reported. In the case of HEAs, the composition space is too large to use DFT to calculate the binding energy of an adsorbate on all possible slabs, so a compromise is made between computation time, accuracy of the calculations and entropy of the data set. The adsorbates of interest are showed in table x:

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

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.?

***High-Entropy Alloy slabs – single-adsorbates***

Explain why these were made and what they are good for

***High-Entropy Alloy slabs – neighbor-adsorbates***

Explain why these were made and what they are good for

***Single-site alloy slabs***

***Single molecules***

In order to compare energies between slabs, slabs with adsorbates and molecules the energies must be calculated from the same DFT code, basis set etc. The energies are sensitive to the basis set, functional and sother DFT calculation factors

***Calculating binding energies***

The reactions of interest in this work are primarily the direct FAOR and the indirect FAOR that results in bound CO, caused by a disproportionation reaction between bound COOH and bound H. In the plot by alexander these are shown

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

Make a nice plot collecting all data – should probably be the size of a full A4 page. Show all Jack’s data and ref and my “own” data. Identical images of all .db’s (used) would be super nice. And a section for the molecules in a powerpointy box section – Pick color scheme

**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:

Simulate a custom surface, for example a standard HEA surface or a surface designed with single-sites. The surfaces have the dimensions 3x200x200.

A voltage is set

**Reactions**

Slabs for testing CO-OH slide reaction – what was the conclusion on this? Seemed unreasonable?

Slabs for estimating H+COOH neighbor interactions

Slabs for estimating swim ring efficiency

Setting reference energies

Energy prediction models for adsorbate binding energies (With HEA and SWR data, hollow-site model, on-top model, mixed-site model) and all the equations and figures of them would be nice

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

Using energy prediction models on simulated surfaces

Plotting them H vs COOH

Bayesian optimization of pair energies – searching for better composition

Coverage simulations and all the logic involved.

The random swim-ring mixture

**Results**

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.

**Conclusion**

Neighbor DFT data

Swim rings

Good composition found?

Method useful?

References

Notes about writing:

In Jack’s thesis he had these headlines between Introduction and Conclusion:

“Catalyst Discovery Using High-Entropy Alloys (?)

Calculating Adsorption Energies with Density Functional Theory (?)

Predicting DFT Adsorption Energies (?)

Optimizing the Composition (?)

Limitations of Methodology (?)”