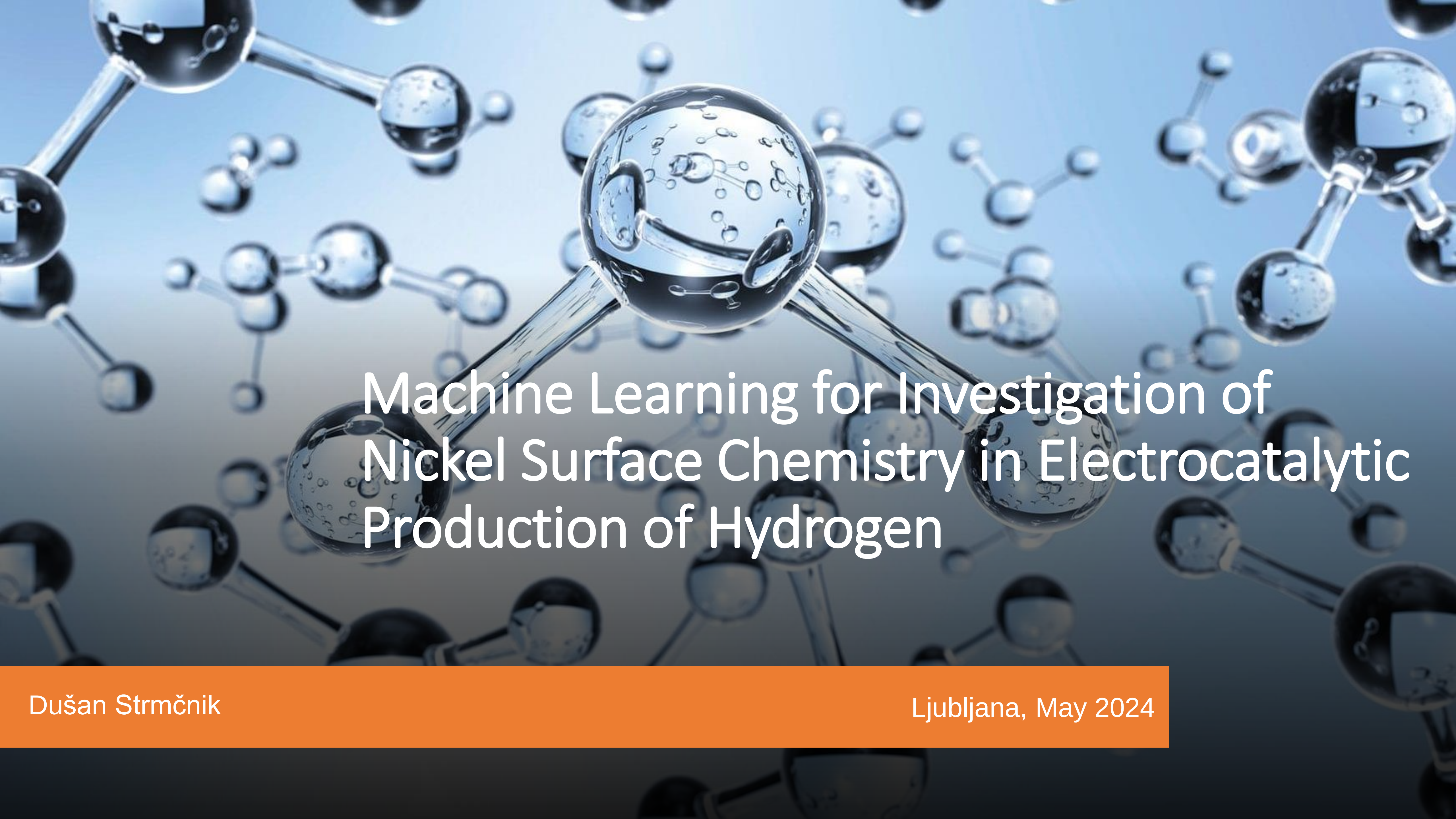

Machine Learning for Investigation of Nickel Surface Chemistry in Electrocatalytic Production of Hydrogen

Dušan Strmčnik

Ljubljana, May 2024

ARIS Funded Fundamental project

Fundamental understanding of Hydrogen Evolution Reaction for a new generation of nickel-based electrocatalysts in alkaline water and chlor-alkali electrolysis

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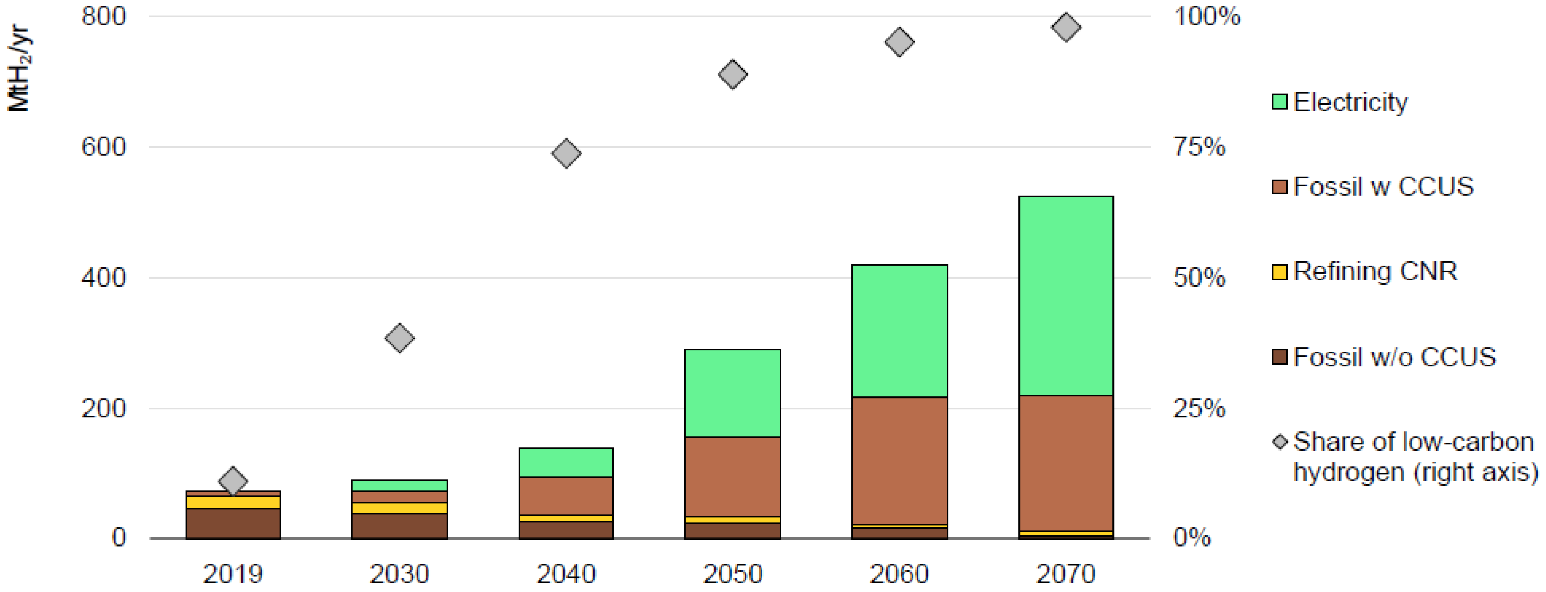
Sašo Džeroski

Motivation - IEA – Energy technology perspectives

Global hydrogen production by technology in the Sustainable Development Scenario, 2019-70



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Note: CNR = hydrogen as by-product from catalytic naphtha reforming in refineries.

Today, hydrogen is produced almost entirely from fossil fuels without CCUS. Low-carbon hydrogen production dominates in the Sustainable Development Scenario, with almost all hydrogen production either from low-carbon electricity or fossil fuels with CCUS.

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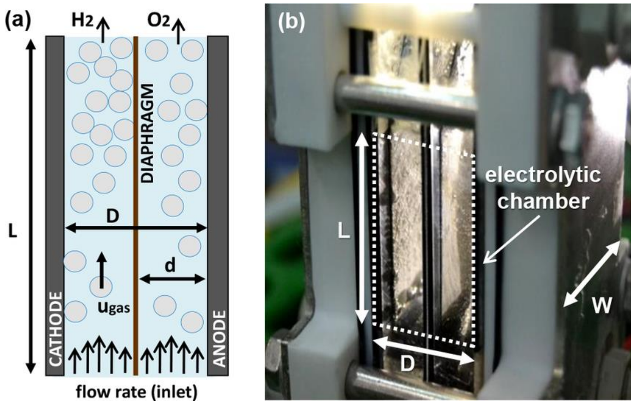
Water electrolysis

Small alkaline water electrolyzer stack



Alkaline water electrolyzer single cell

$$2H_2O \rightarrow 2H_2 + O_2 \qquad \Delta G = -nFE_{cell}$$

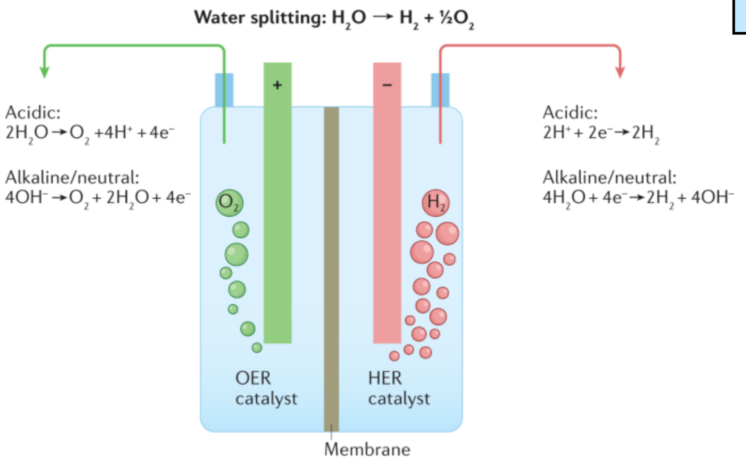
$$\Delta G_{H2O} = -237\ kJ/mol \ \rightarrow\ E_{cell} = 1.23\ V$$

Cathodic branch:

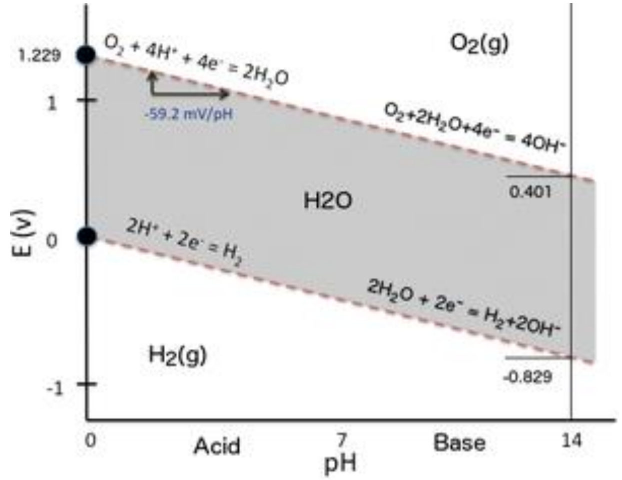
$$4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$$

Anodic branch:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$



Shih, A.J., Monteiro, M.C.O., Dattila, F. *et al.* Water electrolysis. *Nat Rev Methods Primers* **2**, 84 (2022).



Objective(s)

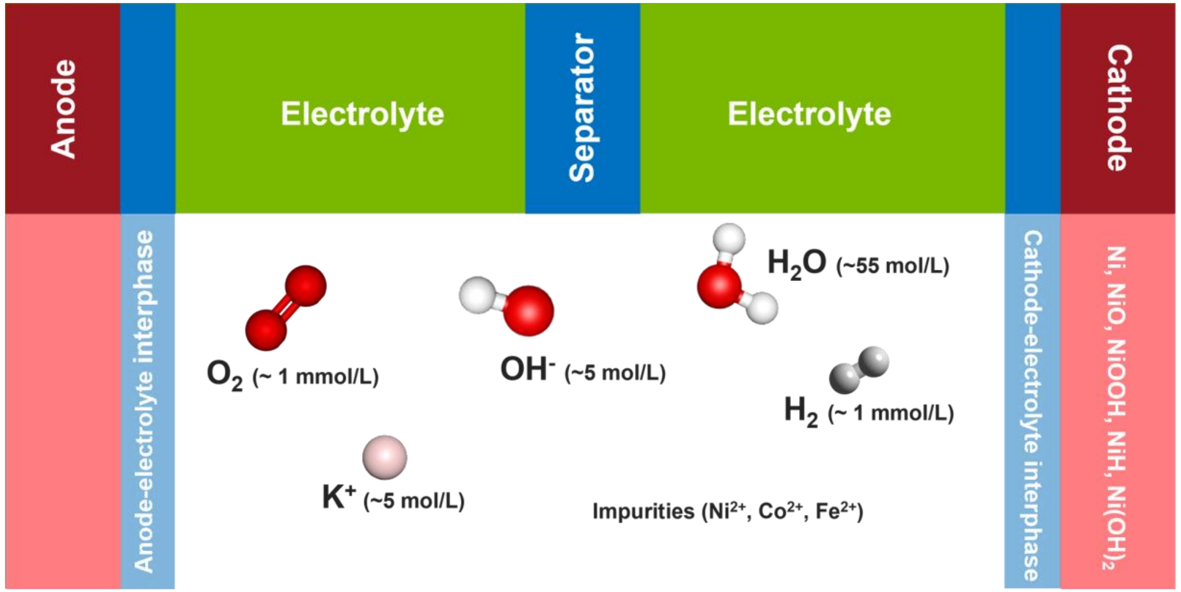
This proposal aims to advance the fundamental understanding of HER on nickel-based cathode catalysts and to utilize this knowledge to develop a new generation of nickel catalysts with 10-times higher activity than state of the art.

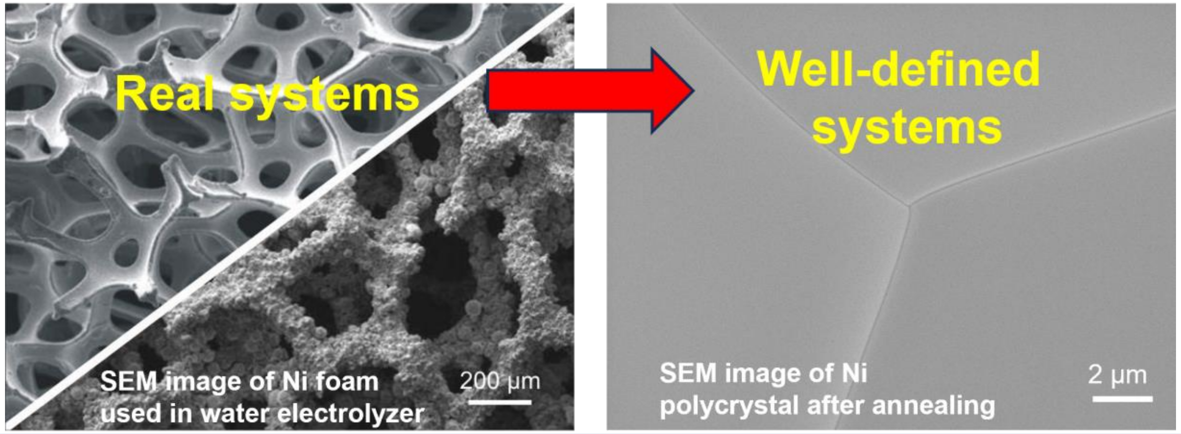
1) What are the active sites for HER on Ni catalysts?
2) What is the role of individual Ni surface species (Ni^0, NiO, $Ni(OH)_2$, Ni(OOH), etc.) in HER electrocatalysis?
3) What is the role of electrolyte pH, cations and anions in HER electrocatalysis on Ni?

Can we find a way to control, influence and alter the electrochemical interface and its properties, instead of just observing and evaluating different combinations of the electrode materials and electrolytes?

Approach

- *The spread of literature-reported catalytic activities for HER on Ni is quite large – a sign of complexity of the system stemming from rich Ni surface chemistry*
- *Simplify complex Ni-based systems to well-defined systems*
- *Develop/utilize several Ni platforms, that connect model to real systems*
- *Develop new tools and methods for the investigation of electrode-electrolyte interphase*
- *Execute detailed analysis of Ni-based materials and electrolyte using established analytical tools and methods (EIS, ToF-SIMS, FTIR, Raman, XPS, RRDE, AFM)*
- *Develop understanding how individual components of the cathode-electrolyte interphase behave at potentials relevant for water electrolysis*
- *Determine intrinsic nickel electrochemical properties over many different nickel platforms, from single atom, over nanoparticles to extended, micro and millimeter size samples.*
- *Develop next generation of materials for HER in alkaline water and chlor-alkali electrolysis*





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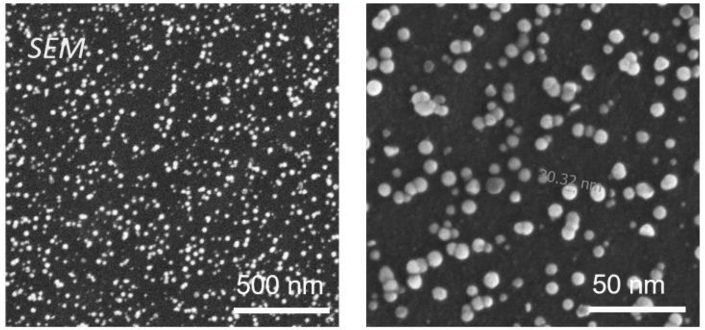
Approach

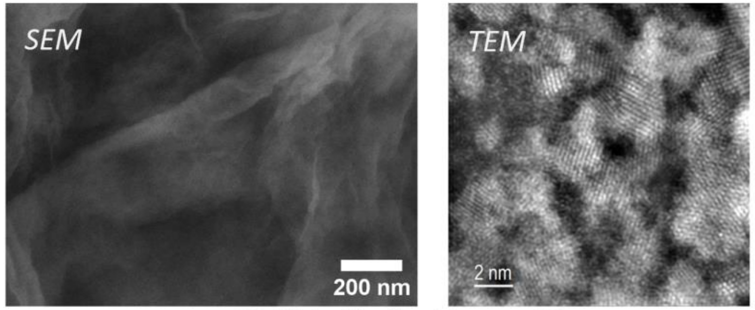
Synthesis of Ni platforms

1. Nickel polycrystal
2. Nickel based nanoparticles (chemically synthesized)
3. Nickel nanoparticles (electrodeposited on GC)
4. Ni TEM grid
5. Ni nano-wires
6. Ni single crystals

Nickel **nanoparticles**
(electrodeposited)

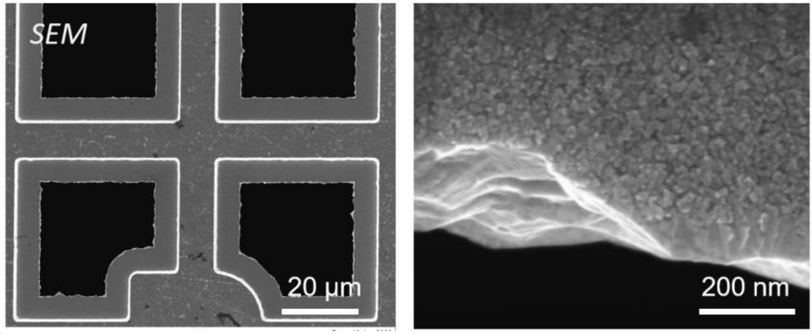


Nickel-based **nanoparticles**
(chemically synthesized)

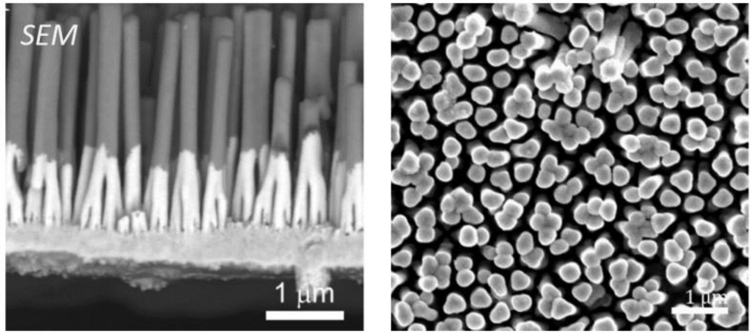


2D Nickel hydroxide on rGO

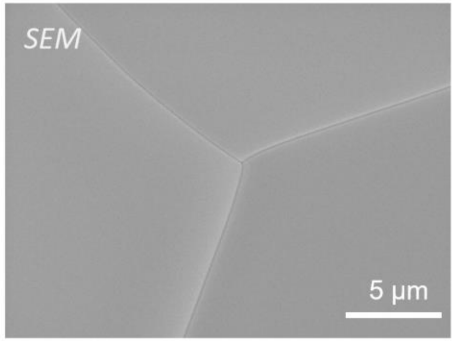
Ni **TEM grid**
(unmodified)



Ni **nano-wires**
(grown using AAO template)



Polycrystalline Ni **disk**
(annealed at 1000°C)



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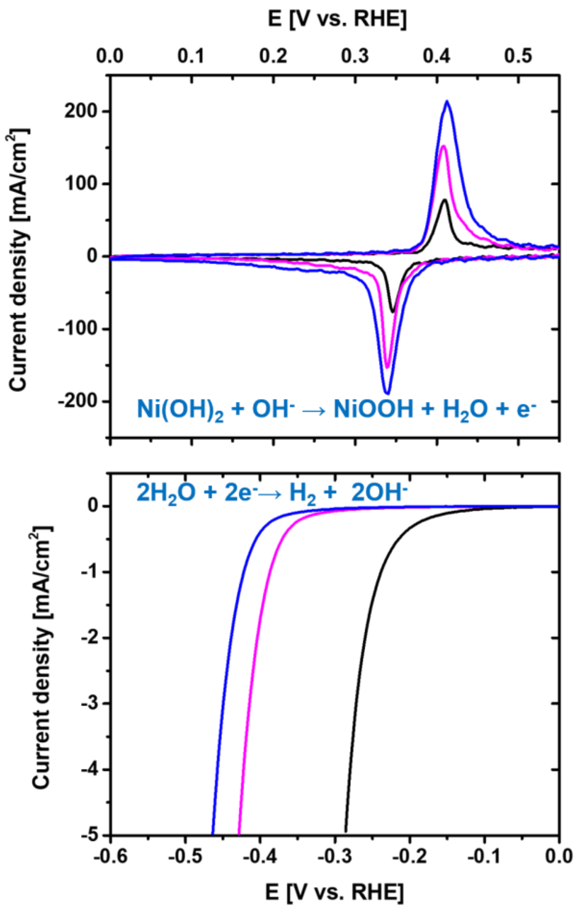
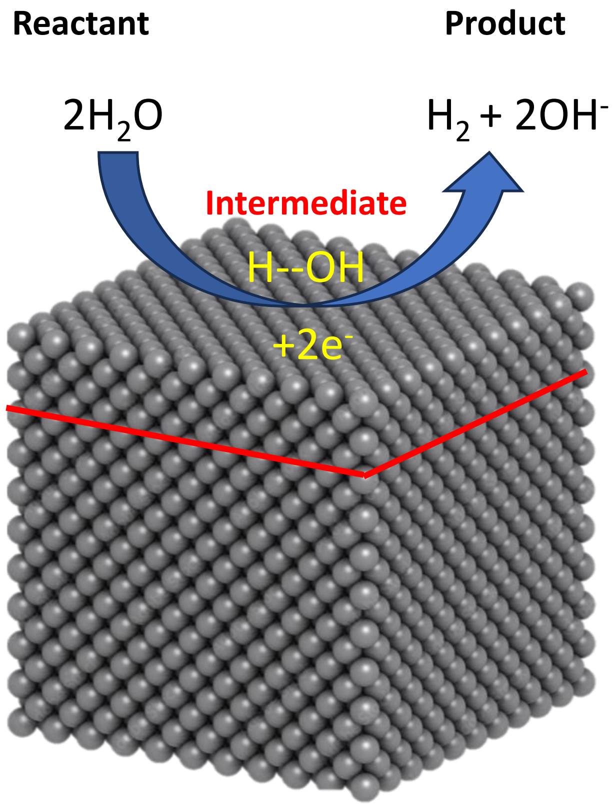
Electrocatalysis happens at the surface





- We are mainly interested in the first few layers of the electrode material.
- Voltammograms give us information about the interaction of electrode material with the electrolyte
- Polarization curves give us information about the catalytic activity of material for a given reaction, e.g. HER
- We want to correlate surface chemistry with electrochemical properties
- We need surface-sensitive analytical tools that provide us with surface composition of the electrode
- One of such tools is ToF-SIMS

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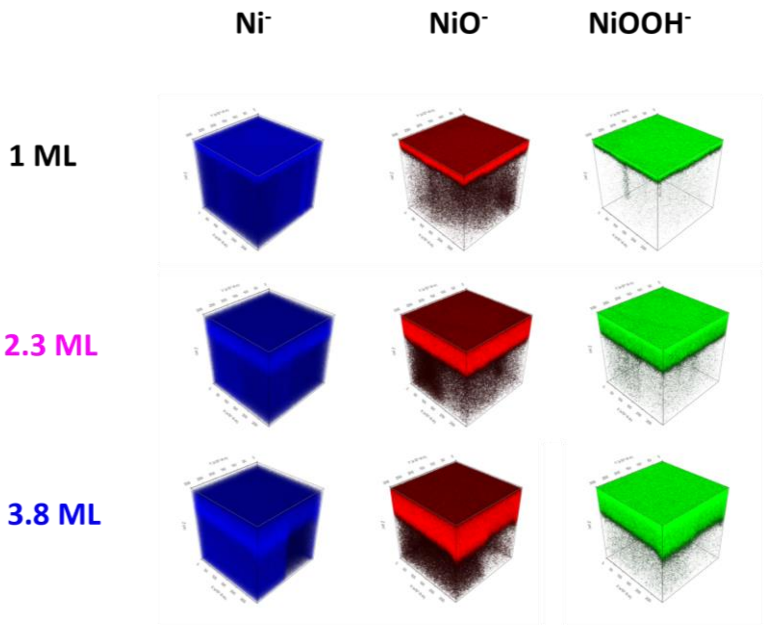
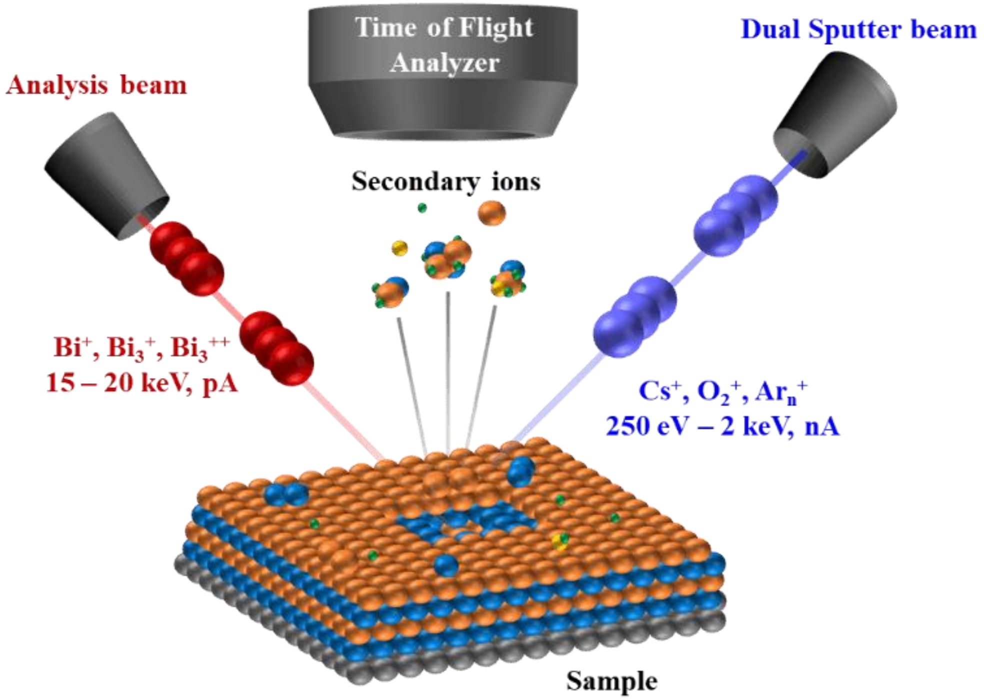
ToF-SIMS

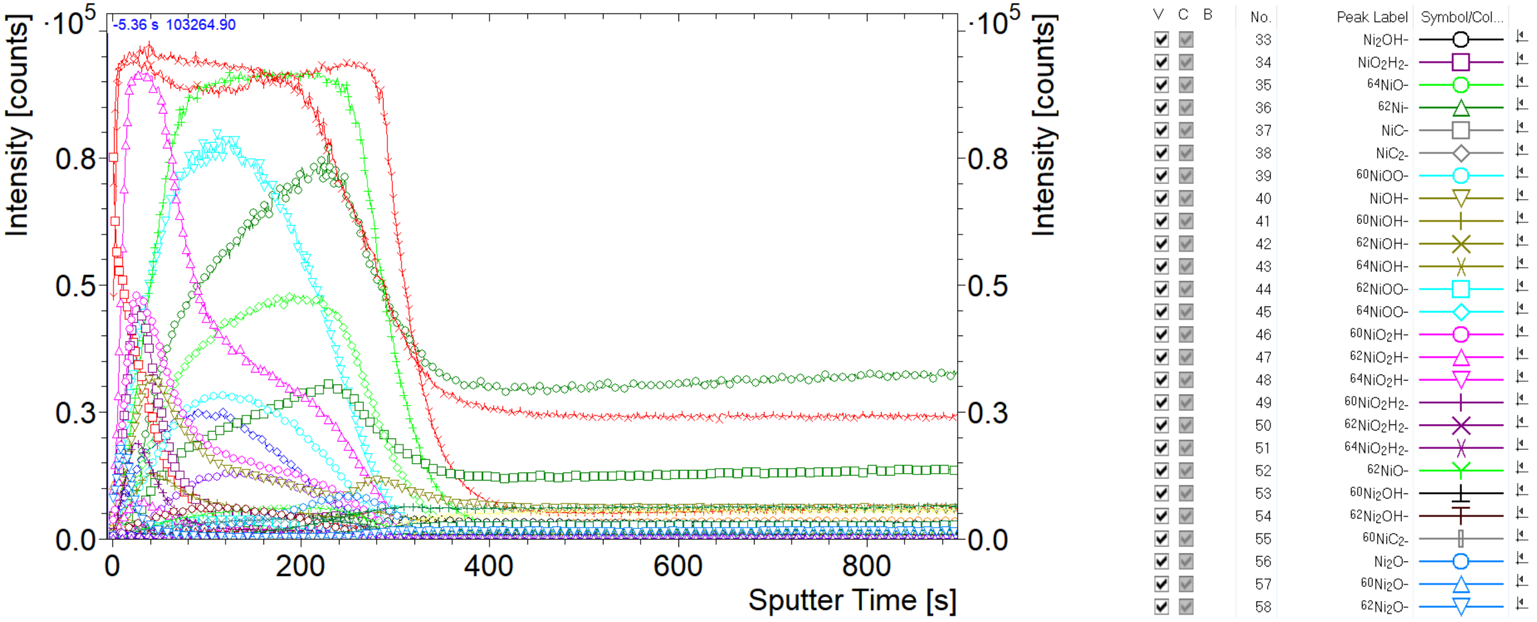




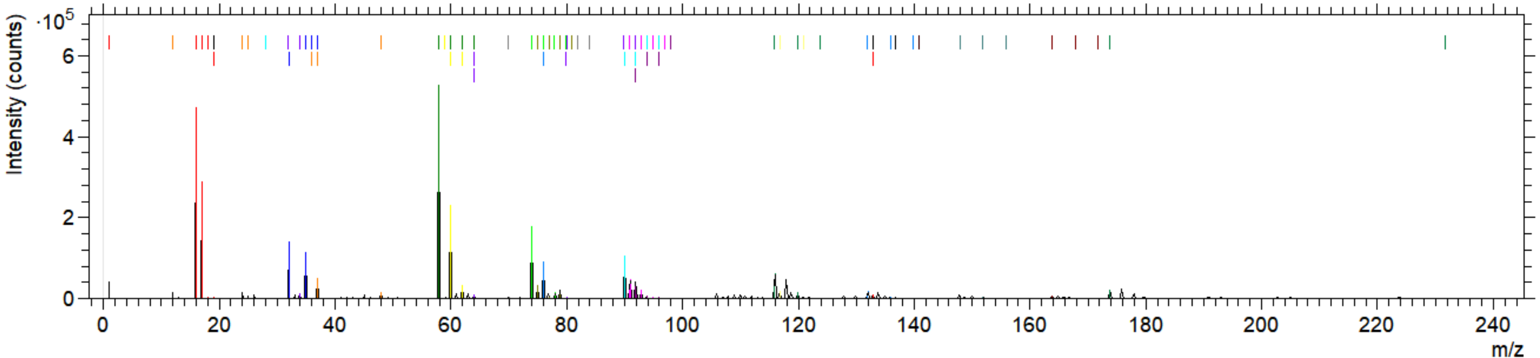
- ToF-SIMS is one of the most sensitive tools available for surface analysis
- It provides information about chemical composition of the sample in 3D with nanometer depth resolution
- Ideal for needle in a haystack problems – we look for fragment with mass of analyte
- However,…

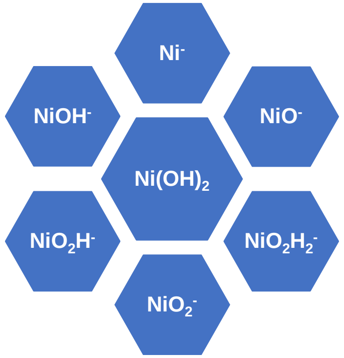
ToF-SIMS data

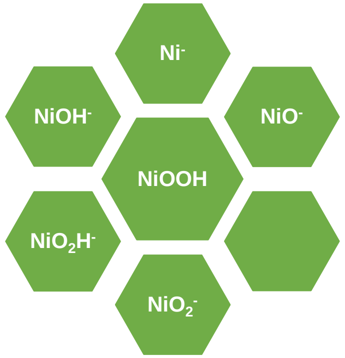
- We collect 500 spectra per depth profile
- In each spectra, there are over 1000 fragments identified
- Each fragment is formed from a species/compound in the sample
- However, same fragment can come from multiple sources and same source can create multiple fragments



V	C	B	No.	Peak Label	Symbol/Col...
☑	☑		33	Ni_2OH^-	○
☑	☑		34	$NiO_2H_2^-$	□
☑	☑		35	$^{64}NiO^-$	○
☑	☑		36	$^{62}Ni^-$	△
☑	☑		37	NiC^-	□
☑	☑		38	NiC_2^-	◇
☑	☑		39	$^{60}NiOO^-$	○
☑	☑		40	$NiOH^-$	▽
☑	☑		41	$^{60}NiOH^-$	+
☑	☑		42	$^{62}NiOH^-$	×
☑	☑		43	$^{64}NiOH^-$	×
☑	☑		44	$^{62}NiOO^-$	□
☑	☑		45	$^{64}NiOO^-$	◇
☑	☑		46	$^{60}NiO_2H^-$	○
☑	☑		47	$^{62}NiO_2H^-$	△
☑	☑		48	$^{64}NiO_2H^-$	▽
☑	☑		49	$^{60}NiO_2H_2^-$	+
☑	☑		50	$^{62}NiO_2H_2^-$	×
☑	☑		51	$^{64}NiO_2H_2^-$	×
☑	☑		52	$^{62}NiO^-$	Y
☑	☑		53	$^{60}Ni_2OH^-$	⊥
☑	☑		54	$^{62}Ni_2OH^-$	⊤
☑	☑		55	$^{60}NiC_2^-$	▯
☑	☑		56	Ni_2O^-	○
☑	☑		57	$^{60}Ni_2O^-$	△
☑	☑		58	$^{62}Ni_2O^-$	▽







Clustering based on correlation matrix

- We find three groups of fragments

C_3^-, C_2H^-, F^-, SO_3^-, C_4^-, C_3H^-, Cl^-, $^{37}Cl^-$, C_5^-, H^-
$^{18}OH^-$, SO_2^-, NiO_2H^-, O^-, Cs^-, $^{60}NiO^-$, NiO^-, S^-, Si^-, AlO^-, $NiOO^-$, $^{18}O^-$, O_2^-,
Zn^-, Ni^-, $^{60}Ni^-$, S_2^-, $^{60}NiH_2^-$, NiH_2^-, OH^-, C_2^-, NiH^-

- First group corresponds to surface contaminants during sample transfer
- Second group corresponds to the interfacial film grown electrochemically
- Third group corresponds to the bulk of the sample

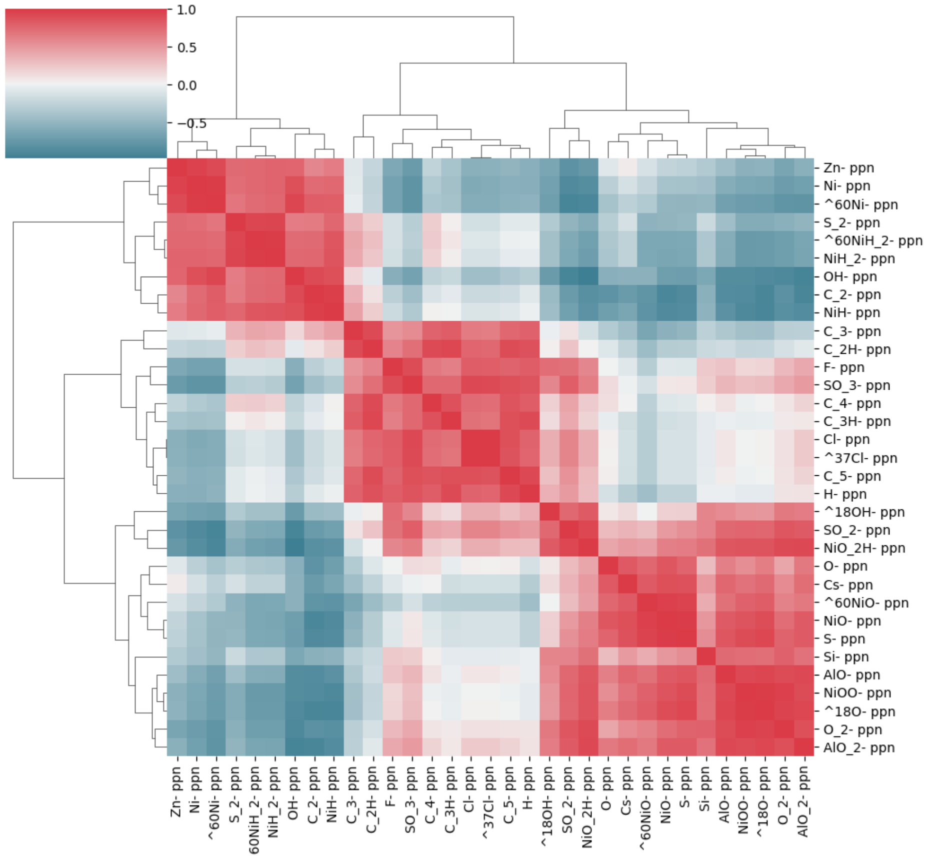
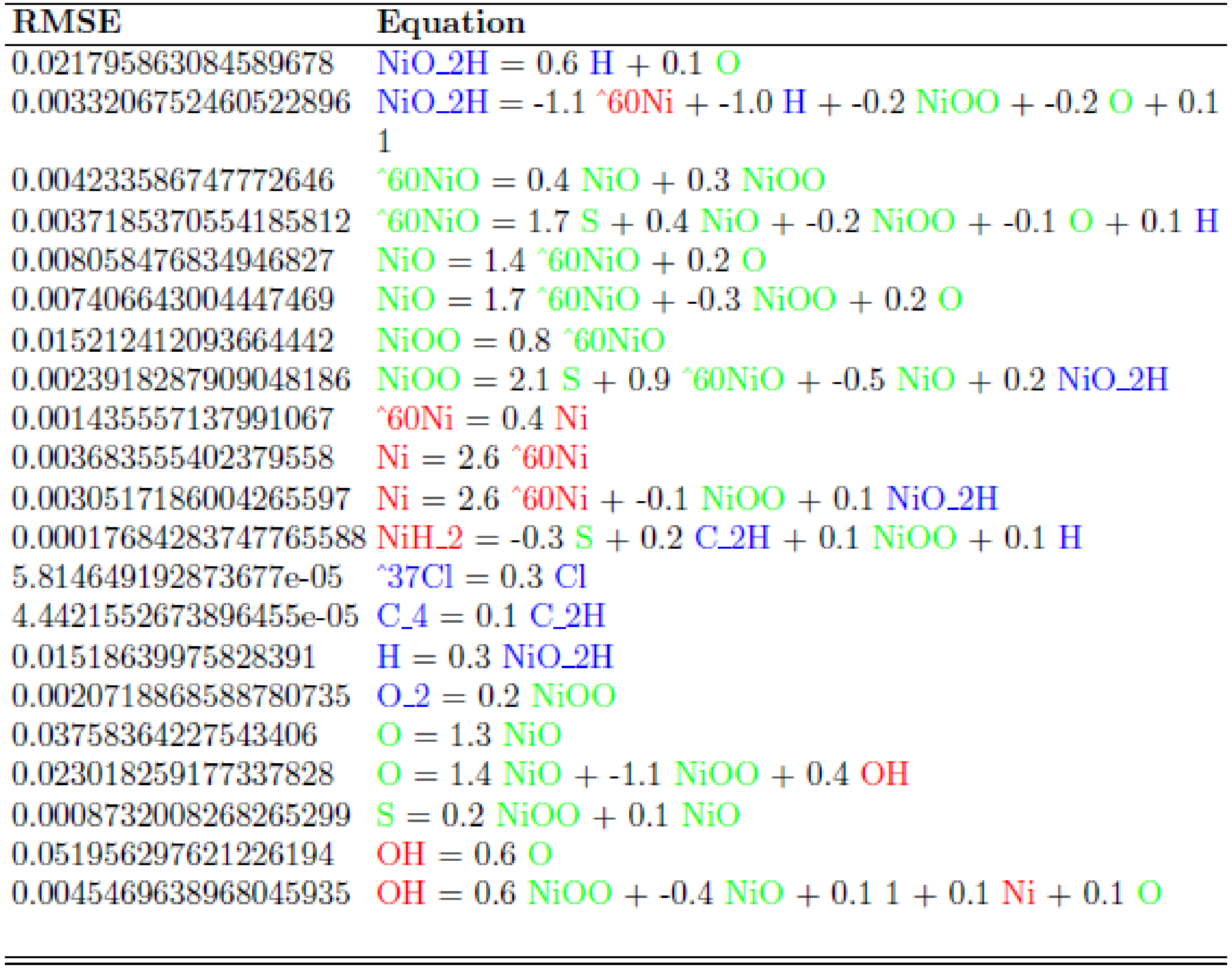


Fig. 1. The result of hierarchical clustering, which is based on a correlation matrix (i.e.,distance determined by Spearman's coefficient of correlation) between the fragment concentrations. It highlights three prominent clusters (represented by red squares).

Equation discovery

- We use the symbolic regression method SINDy to identify mathematical relations between the fragments' intensities in mass spectra
- We work under the assumption that each fragment can be written as a linear combination of the other fragments
- We have some naturally built-in controls, i.e. isotope ratios, which the method identifies
- It also gives several nonsensical correlations and a few that need to be further investigated



RMSE	**Equation**
0.021795863084589678	NiO_2H = 0.6 H + 0.1 O
0.0033206752460522896	NiO_2H = -1.1 ^60Ni + -1.0 H + -0.2 NiOO + -0.2 O + 0.1 1
0.004233586747772646	^60NiO = 0.4 NiO + 0.3 NiOO
0.0037185370554185812	^60NiO = 1.7 S + 0.4 NiO + -0.2 NiOO + -0.1 O + 0.1 H
0.008058476834946827	NiO = 1.4 ^60NiO + 0.2 O
0.007406643004447469	NiO = 1.7 ^60NiO + -0.3 NiOO + 0.2 O
0.015212412093664442	NiOO = 0.8 ^60NiO
0.0023918287909048186	NiOO = 2.1 S + 0.9 ^60NiO + -0.5 NiO + 0.2 NiO_2H
0.001435557137991067	^60Ni = 0.4 Ni
0.003683555402379558	Ni = 2.6 ^60Ni
0.0030517186004265597	Ni = 2.6 ^60Ni + -0.1 NiOO + 0.1 NiO_2H
0.00017684283747765588	NiH_2 = -0.3 S + 0.2 C_2H + 0.1 NiOO + 0.1 H
5.814649192873677e-05	^37Cl = 0.3 Cl
4.4421552673896455e-05	C_4 = 0.1 C_2H
0.01518639975828391	H = 0.3 NiO_2H
0.0020718868588780735	O_2 = 0.2 NiOO
0.03758364227543406	O = 1.3 NiO
0.023018259177337828	O = 1.4 NiO + -1.1 NiOO + 0.4 OH
0.0008732008268265299	S = 0.2 NiOO + 0.1 NiO
0.051956297621226194	OH = 0.6 O
0.0045469638968045935	OH = 0.6 NiOO + -0.4 NiO + 0.1 1 + 0.1 Ni + 0.1 O

Conclusions

- Initial application of machine learning methods on ToF-SIMS data has given some encouraging preliminary results

- Clustering of fragments shows logical distribution of species within the electrochemical interface, significantly reducing time of similar analysis if done by user

- Equation discovery needs further improvement, most likely better initial guidance, but we also need some improvements in spectra collection and sample preparation

- Quality of data is the most important factor in successful implementation of ML methods

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Thank you!