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Experimental approach for generating data for model verification

CompBat-Sonar workshop

27 June 2022

UPPSALA UNIVERSITET

UNIVERSITÀ DI PISA

Aalto University School of Chemical Engineering

JYVÄSKYLÄN YLIOPISTO UNIVERSITY OF JYVÄSKYLÄ

ttk

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Experimental approach for generating data for model verification

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IN SUPREMÆ DIGNITATIS 1343

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CompBat WP4

CompBat: Developing tools for discovery of new prospective candidates for next generation RFBs

WP4: Model validation and experimental data generation

Main objective: High quality data generation for verifying the models

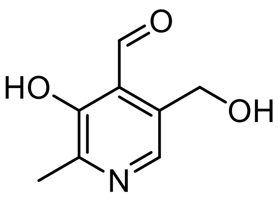
Strategy: Synthesis of key candidates → electrochemical testing → cell and short stack testing

Partners involved: UTU, JYU, TTK, UU, UNIPI, SKOLTECH

Pyridoxal database

Pyridoxal database

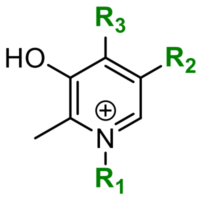
bioinspired AO RFBs



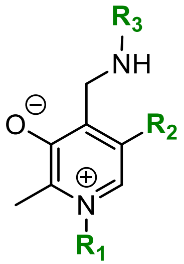
pyridoxal

(vitamin B_6)

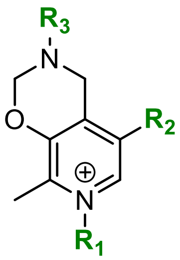
6712 molecules



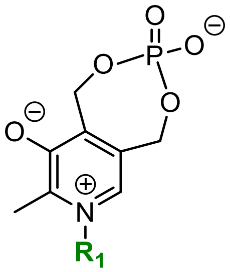
pyr1



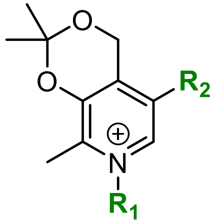
pyr2



pyr3

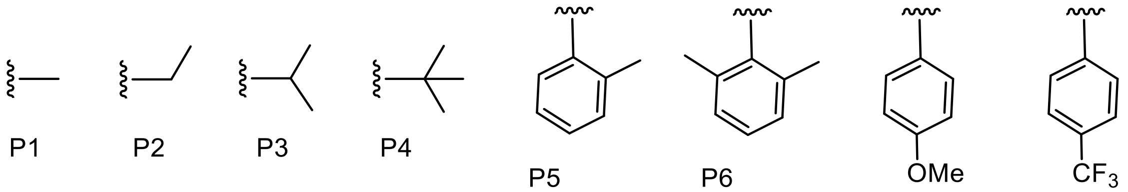


pyr4



pyr5

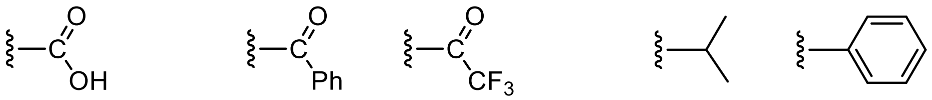
R_1 :



P1 P2 P3 P4 P5 P6 P7 P8

R_2 : 113 different substituents (a1, a2, ..., b1, b2, ..., etc)

R_3 :

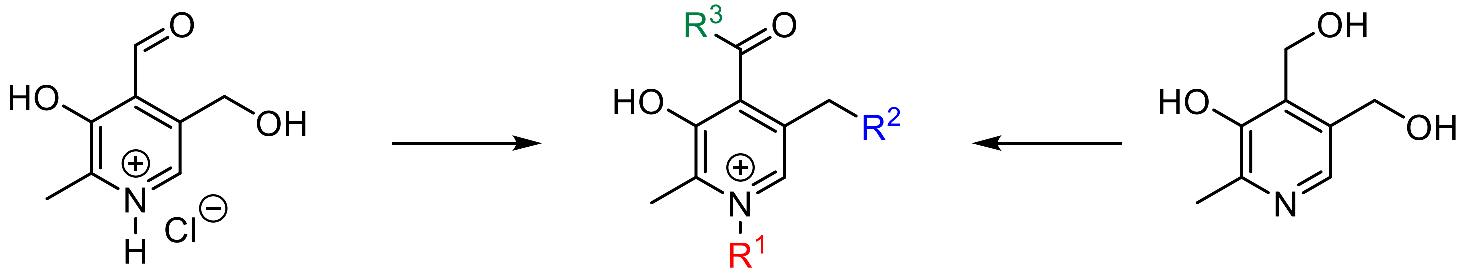


A B C D E

(in pyr1) (in pyr1 and pyr2) (in pyr3)

Organic synthesis (JYU)

- **Goal**: Establish a synthetic route to the pyridoxine/pyridoxal core battery materials.
- This will assist in answering the following key questions:
  - whether the pyridoxal/pyridoxine core has the desired redox potential and stability for RFB cycles
  - which factors, such as substitution patterns, affect these properties



Pyridoxal hydrochloride **Desired RFB molecule sets** Pyridoxine

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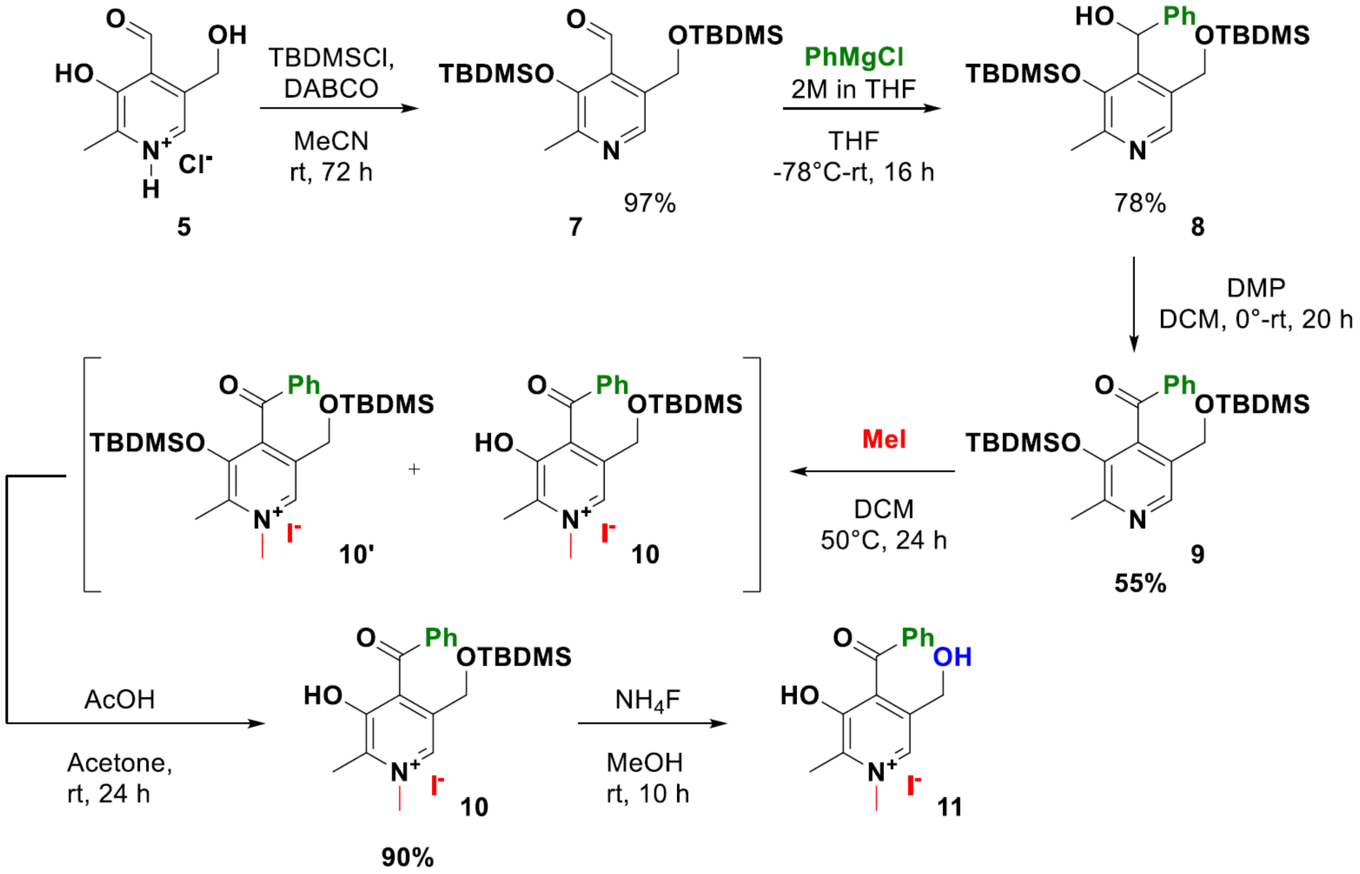
Synthetic approach



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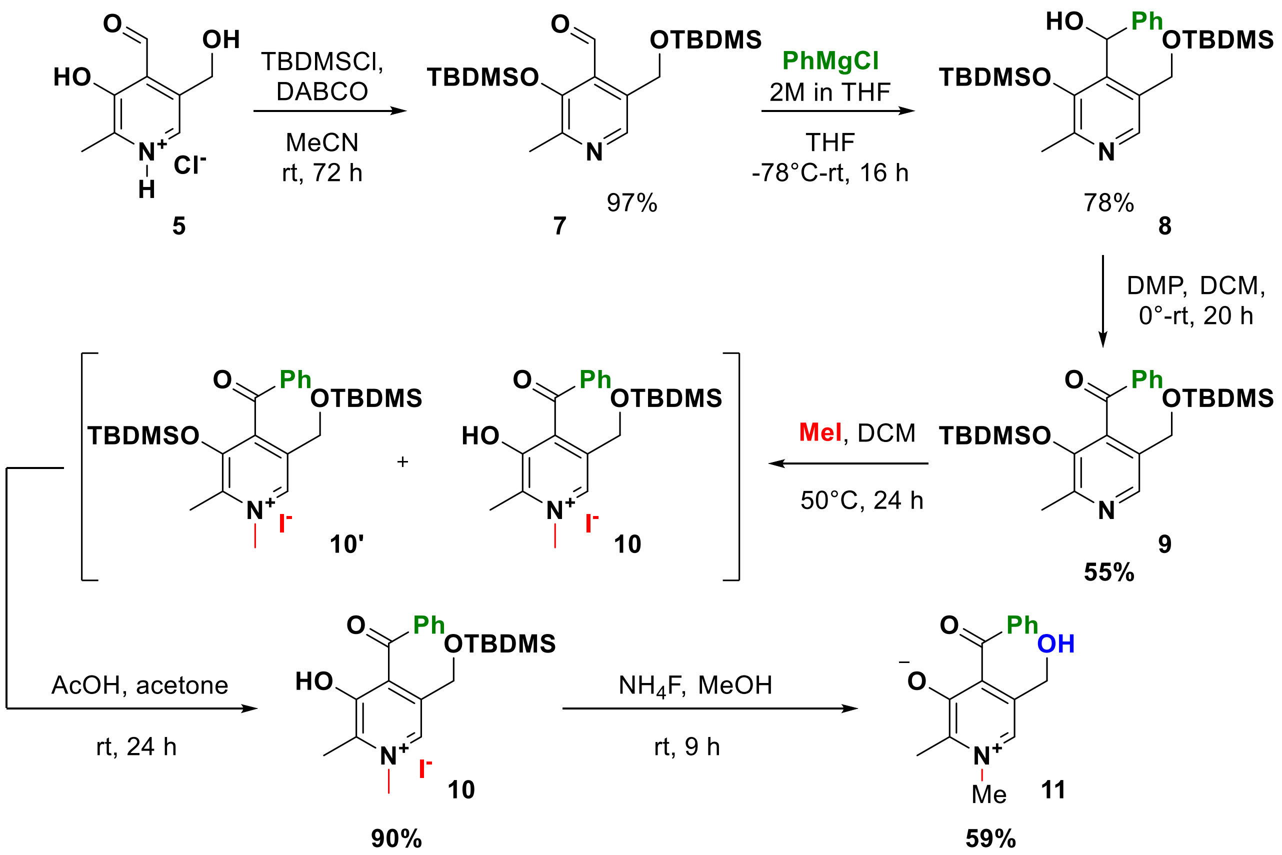
Organic synthesis (JYU)

- Silyl protection (TBDMS) of pyridoxal is the key step in the synthesis of ketone subfamily of the molecules. We have synthesized our first ketone derivative **11** in five synthetic steps.



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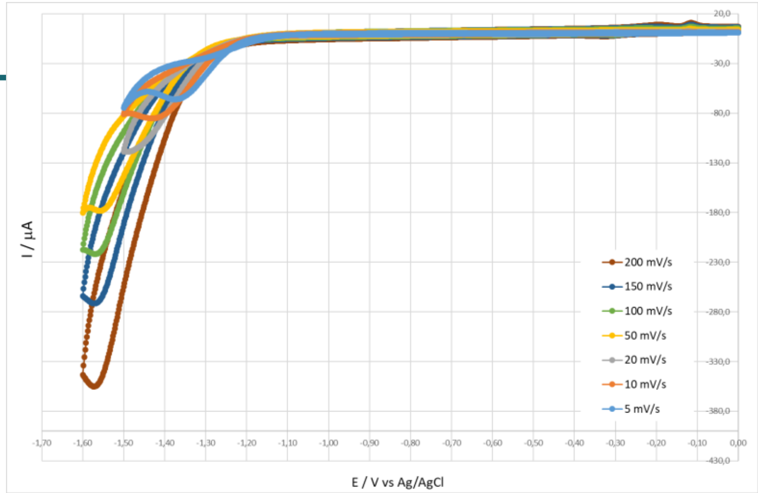
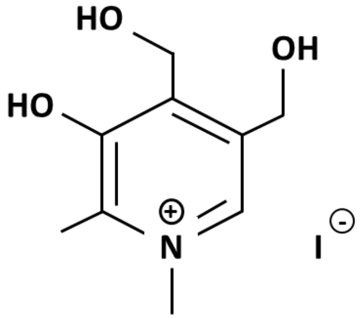
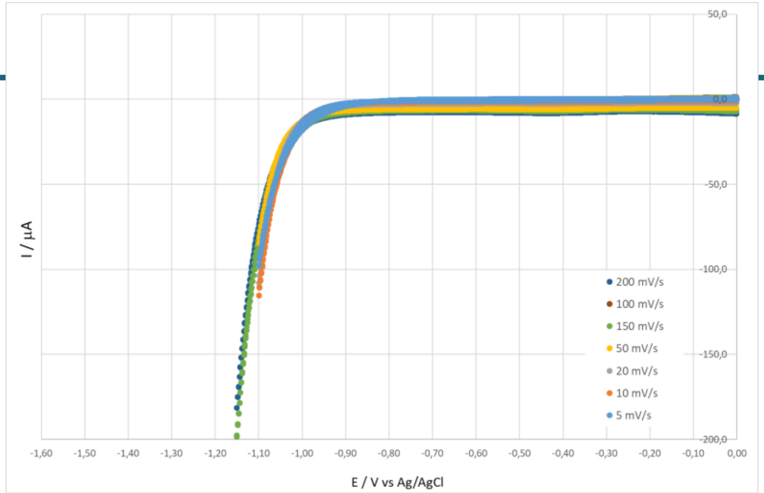
TESTING NEW MATERIALS COMPOUNDS SYNTHETIZED IN JYVÄSKYLÄ

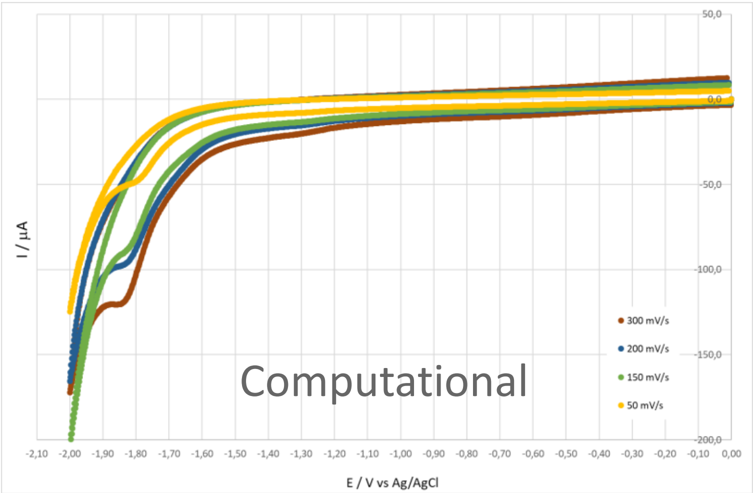


1 mM in 1 M KCl – pH 7





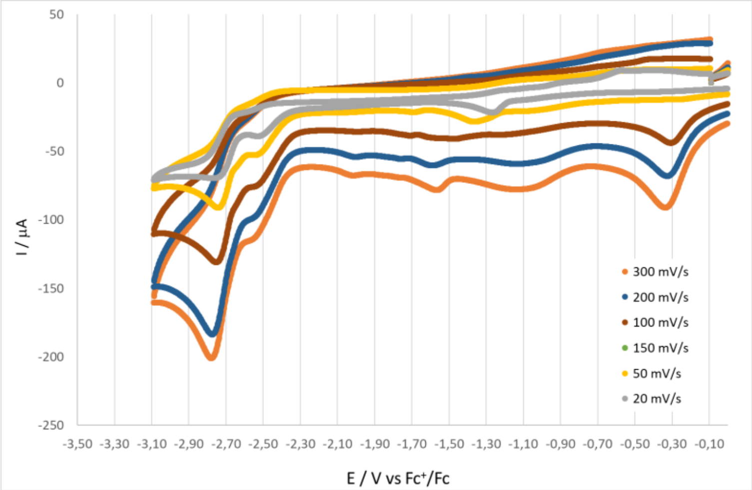
1 mM in 0,1 M H_2SO_4



1 mM in 0,1 M NaOH

Computational:
-2.2 V vs. Ag/AgCl

Not stable



1 mM in Acetonitrile - TBAP 0,1 M

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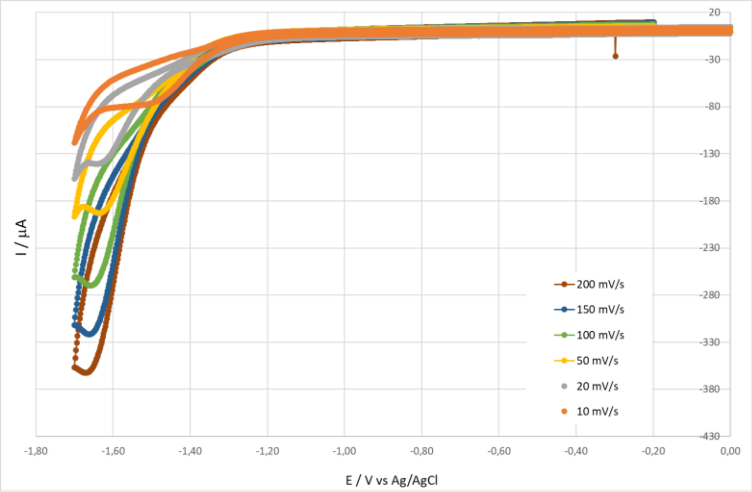
TESTING NEW MATERIALS COMPOUNDS SYNTHETIZED IN JYVÄSKYLÄ



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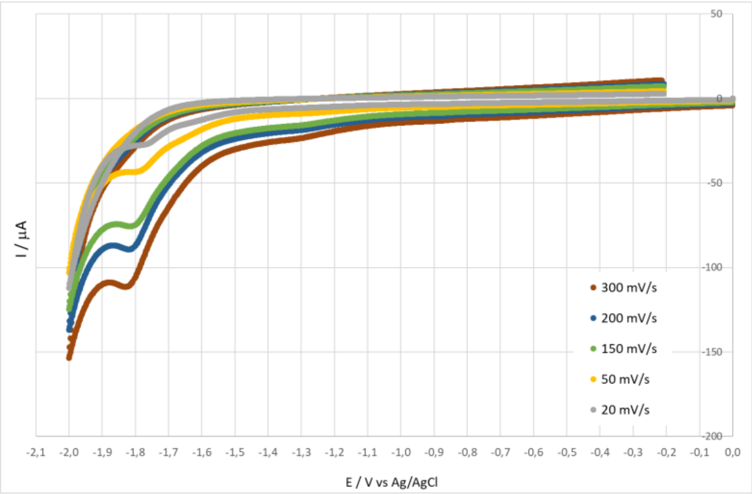
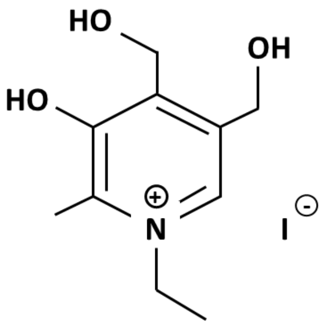
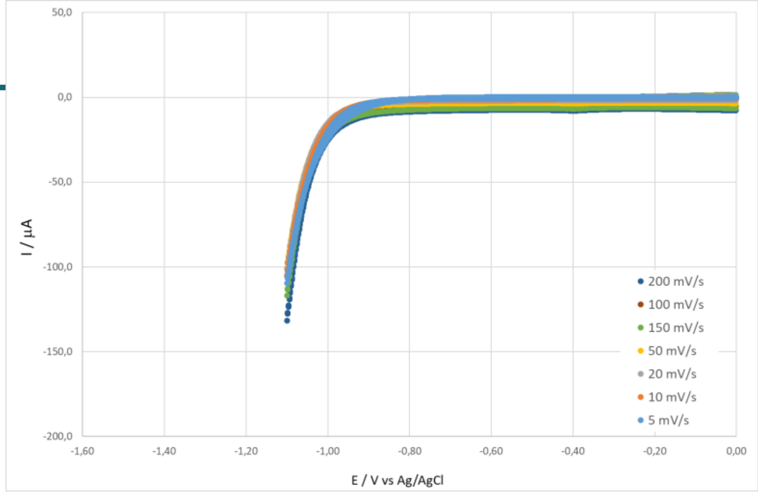


1 mM in 0,1 M NaOH



Computational:
-2.14 V vs. Ag/AgCl

Not stable



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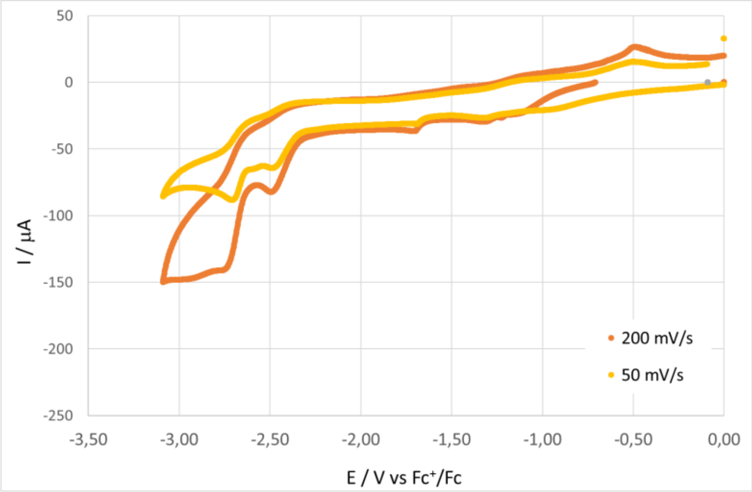

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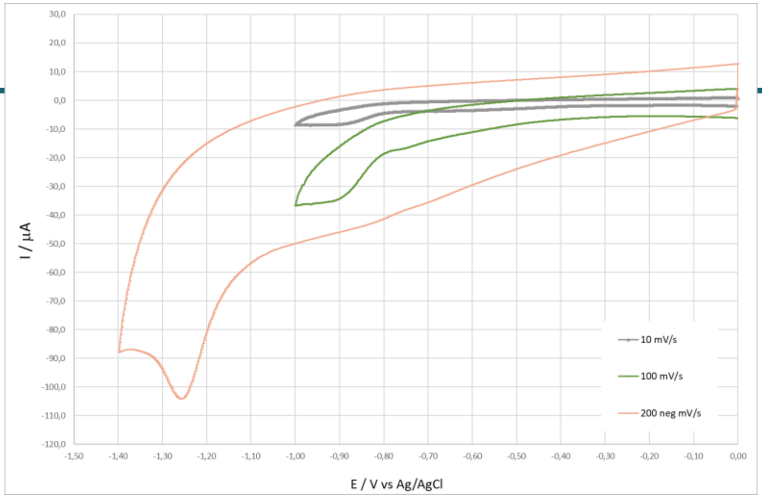
TESTING NEW MATERIALS COMPOUNDS SYNTHETIZED IN JYVÄSKYLÄ



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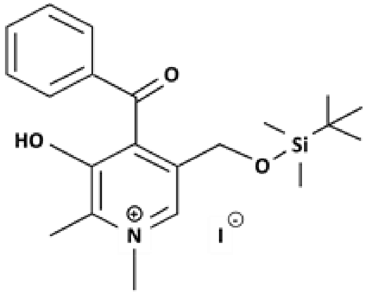

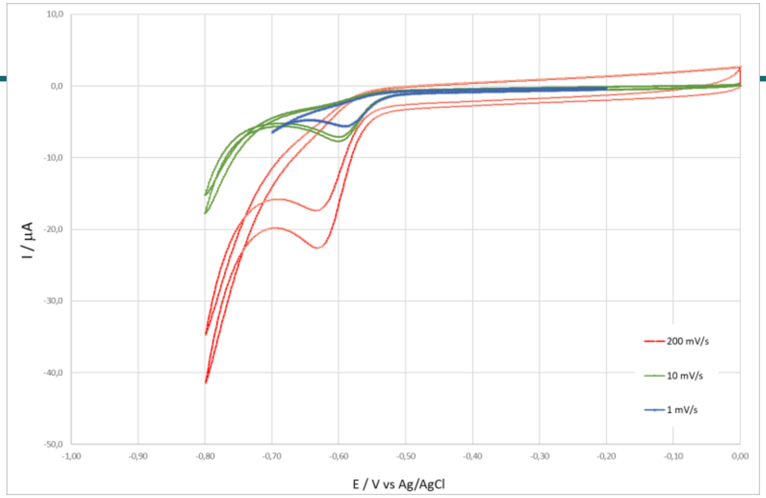

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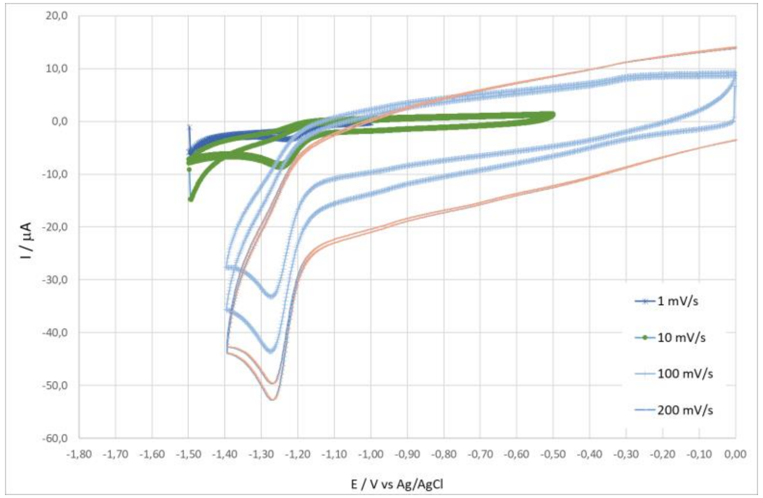
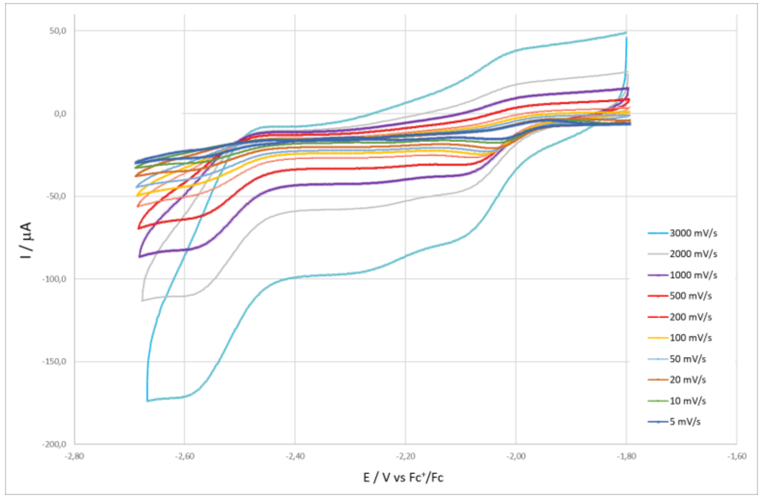


1 mM in 0,1 M NaOH

Computational:
-1.57 V vs. Ag/AgCl
or -1.77 V vs. Ag/AgCl
for hydrolyzed version

Slighly more stable



1 mM in Acetonitrile - TBAP 0,1 M

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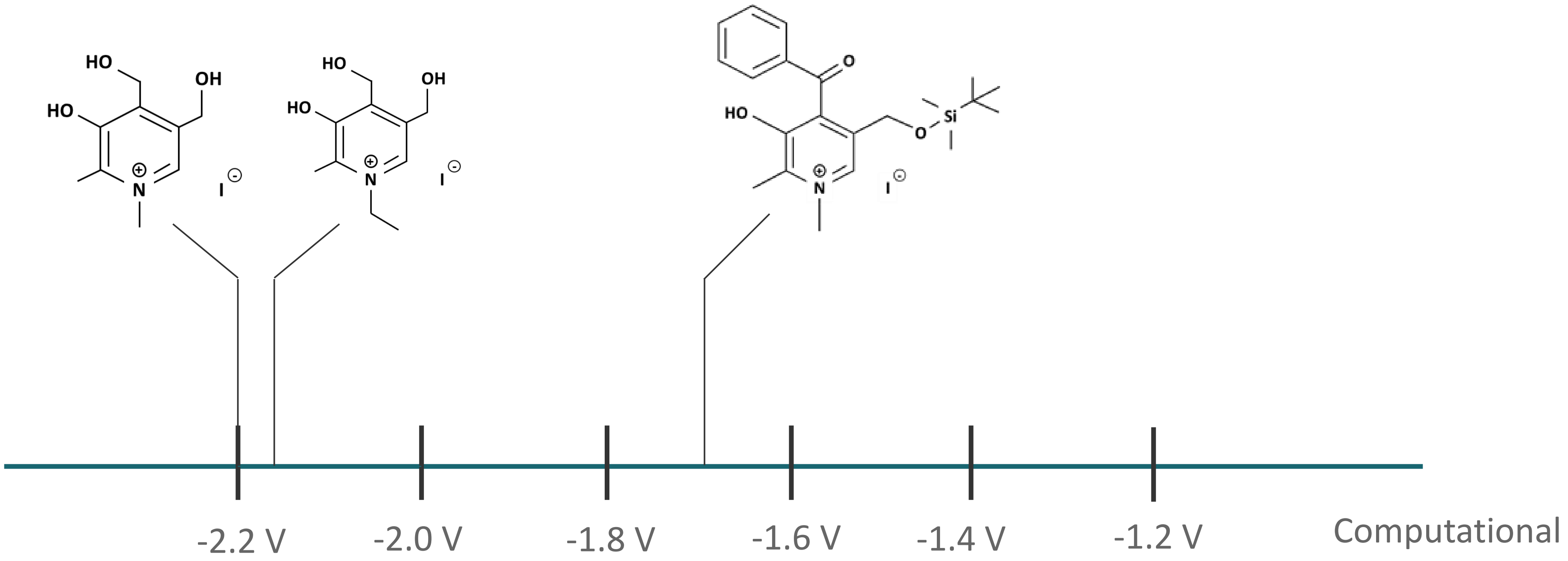
Conclusions

- Computed trends for redox potentials reproduced in the experiments



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Conclusions

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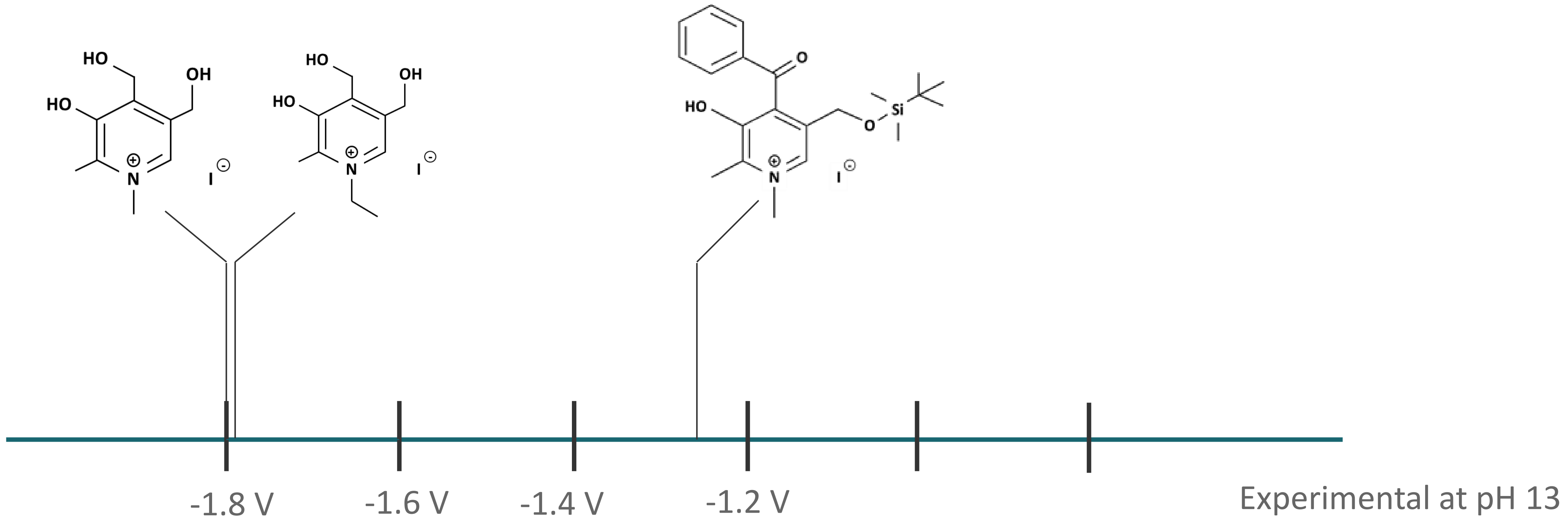

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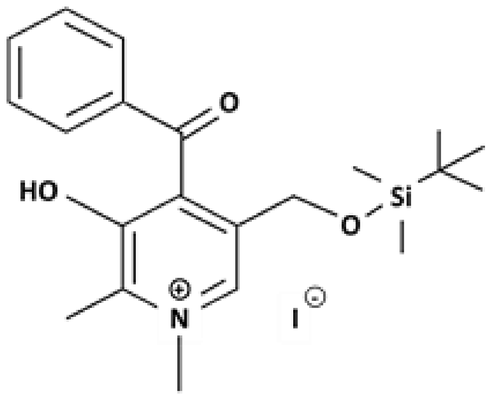
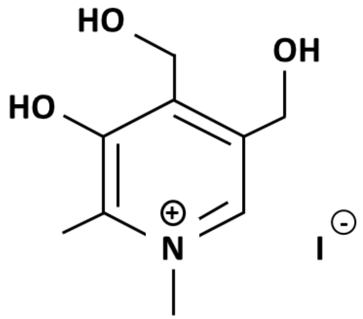
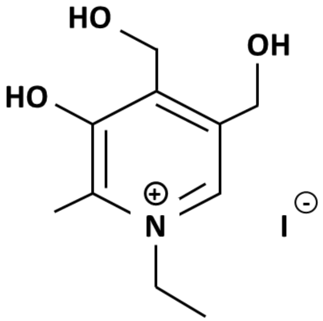
Conclusions



More stable





Unstable

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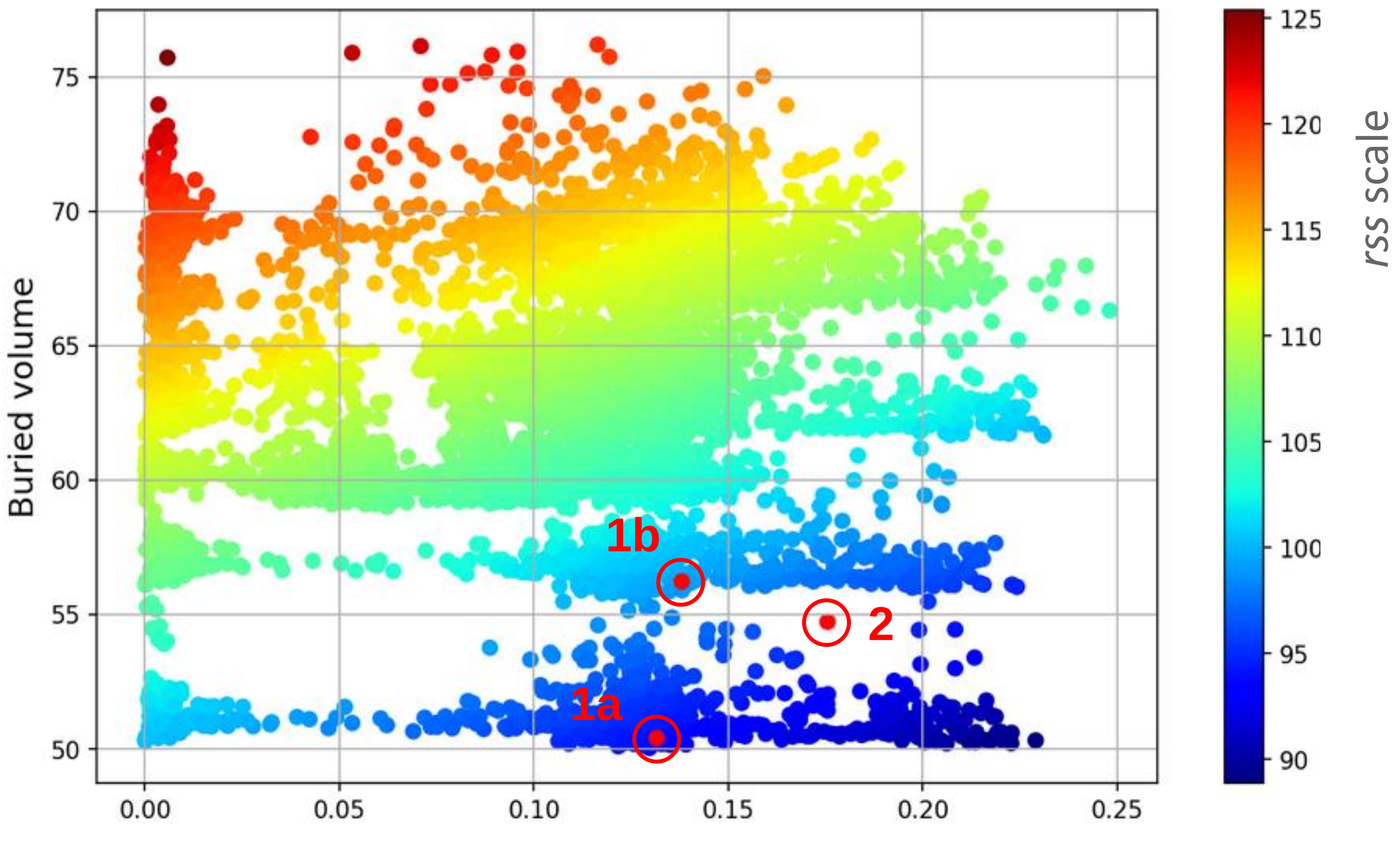
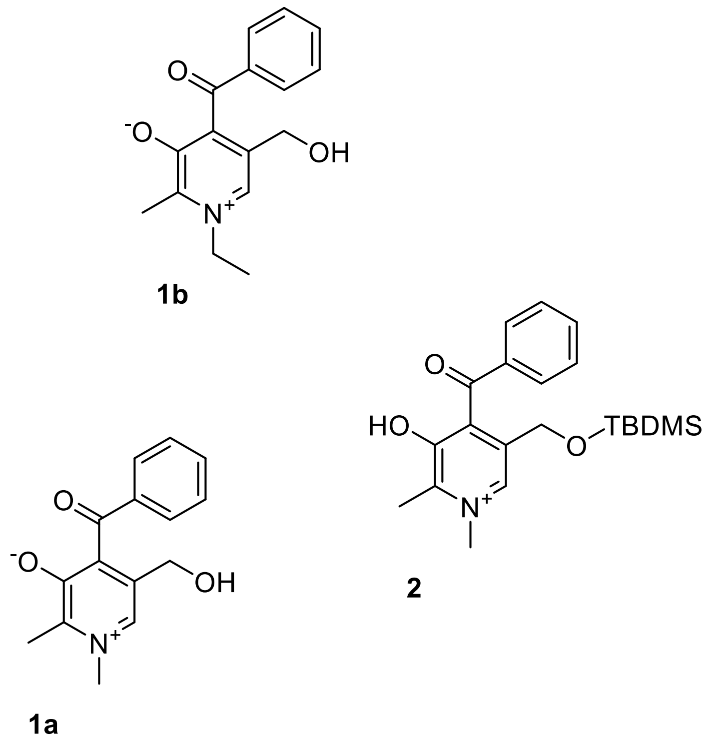
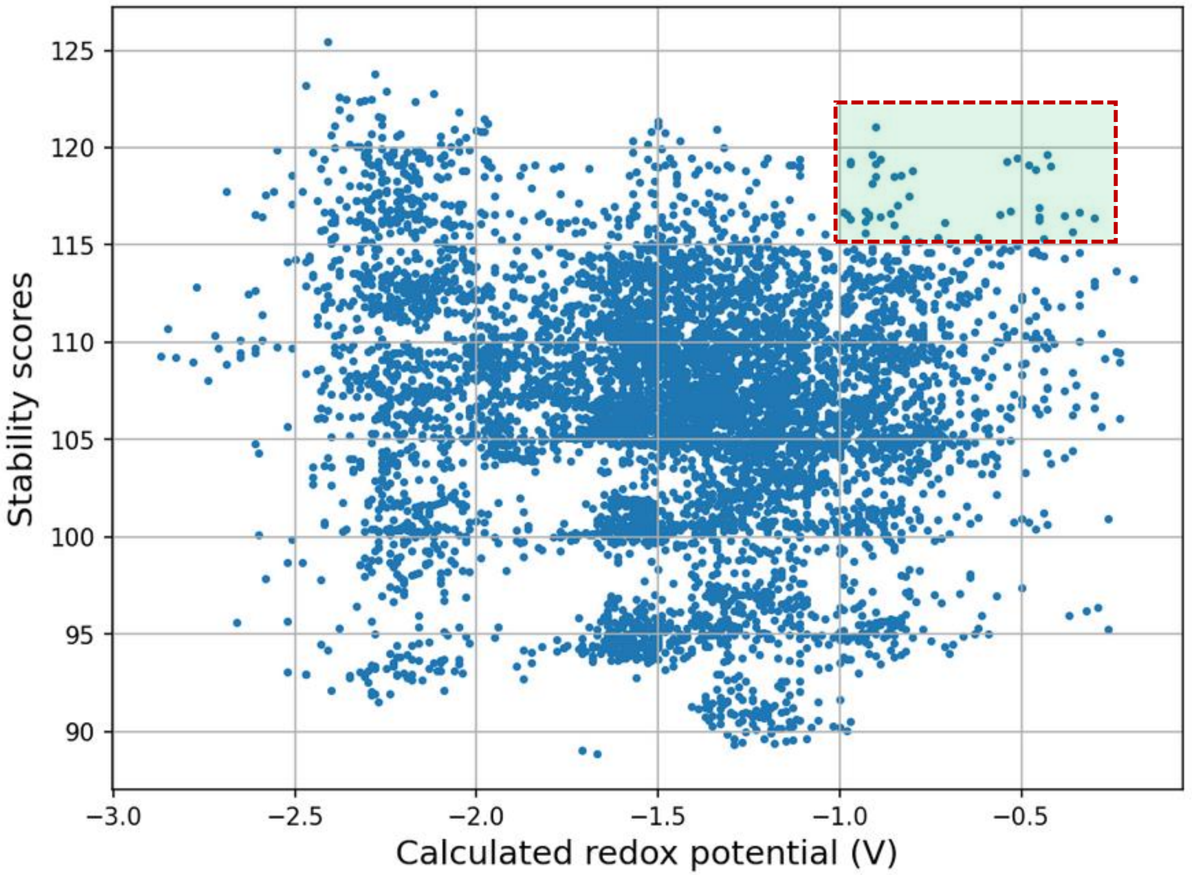
Analysis of PYR database

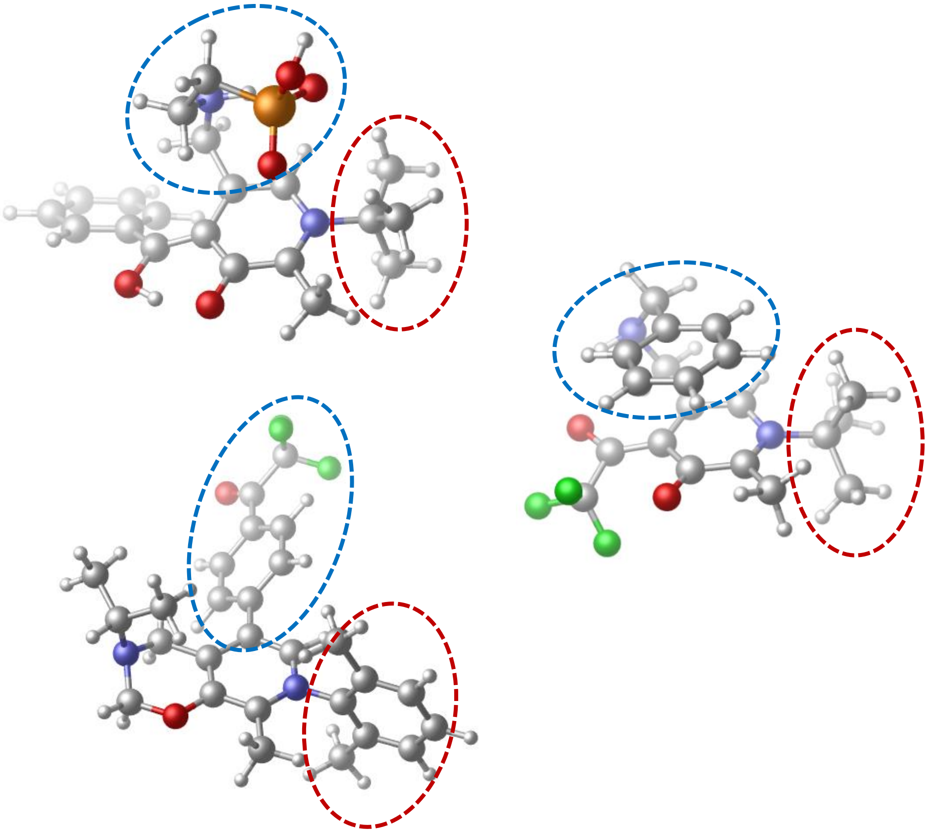




Stability studies

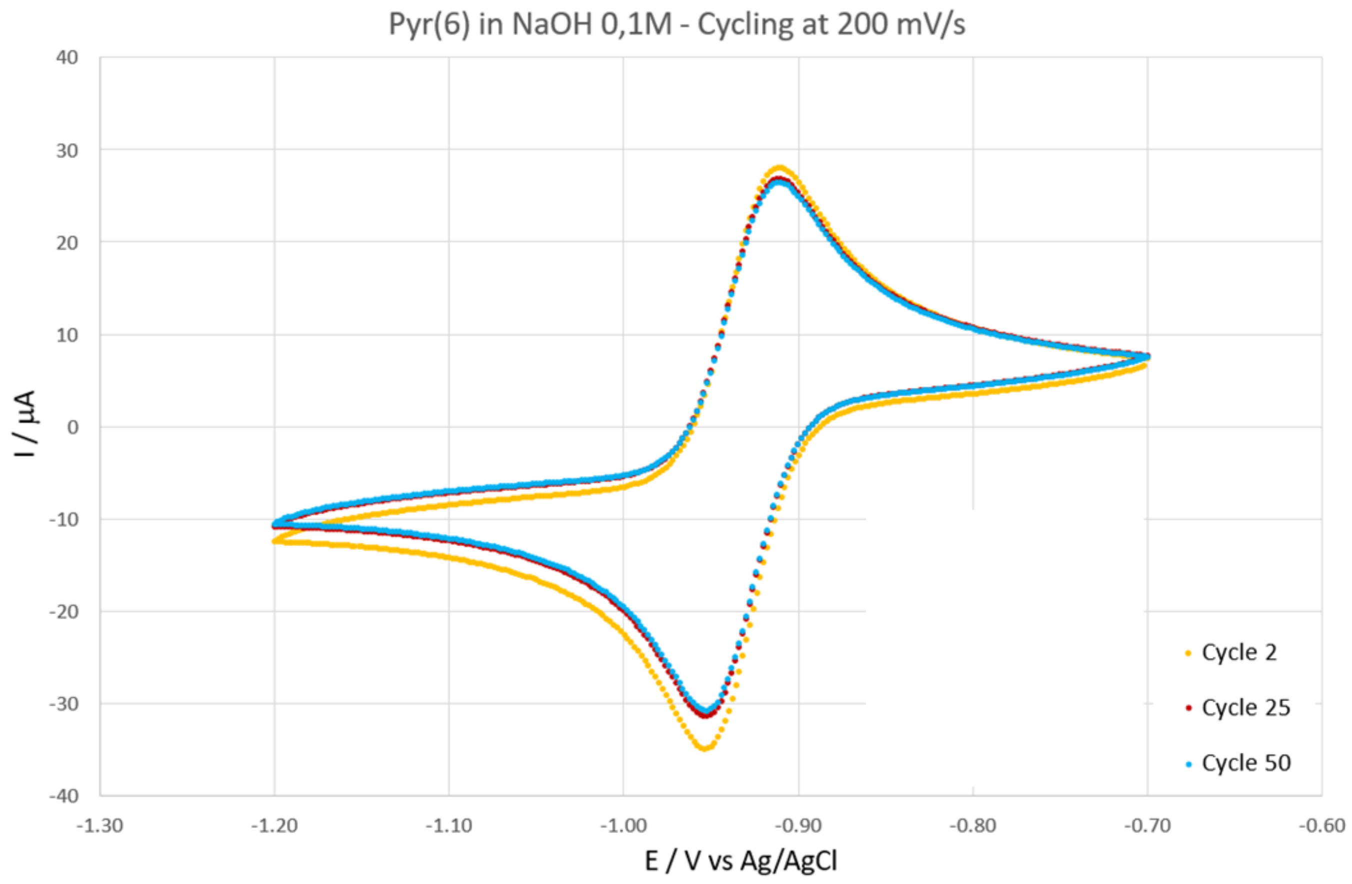
Analysis of PYR database



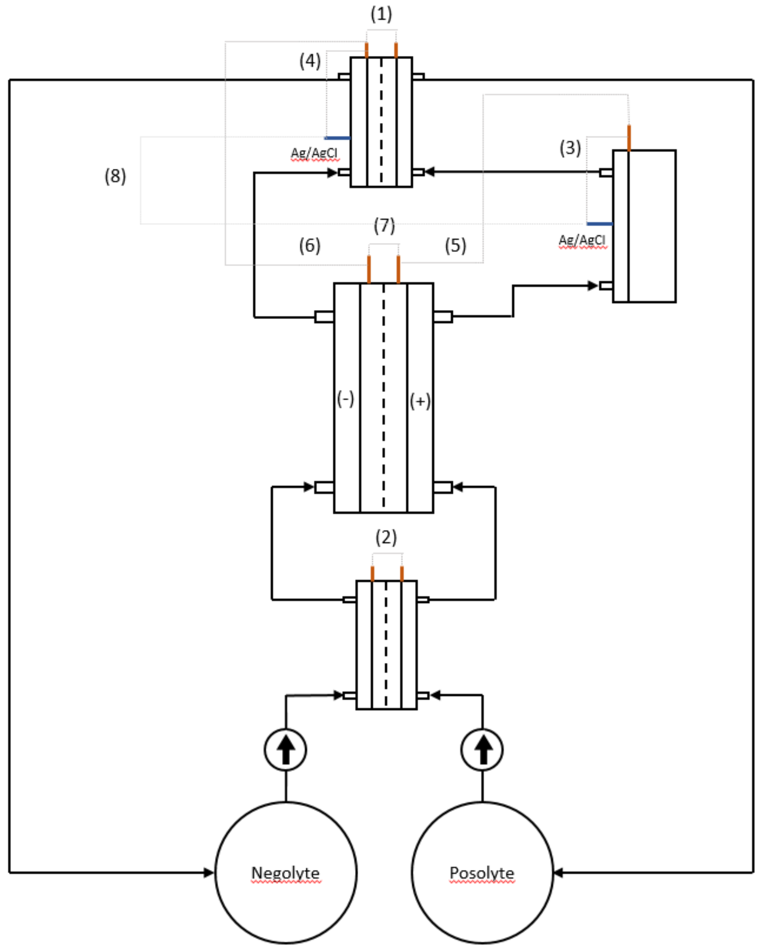


bulky R_1 and R_2

Stable molecule synthesized



Flow battery test bench



1. Open circuit potential after the main cell.
2. Open circuit potential before the main cell.
3. Potential of the Positive Electrode against Reference Electrode Ag/AgCl
4. Potential of the Negative Electrode against Reference Electrode Ag/AgCl
5. Potential of the Positive Electrode after the main cell against the potential of the Positive Electrode in the main cell (Positive Electrode polarization).
6. Potential of the negative Electrode after the main cell against the potential of the Negative Electrode in the main cell (Negative Electrode polarization).
7. Main Cell potential and current density
8. Potential of the Reference Electrode of the Positive side against the Reference Electrode of the Negative side (membrane potential drop).

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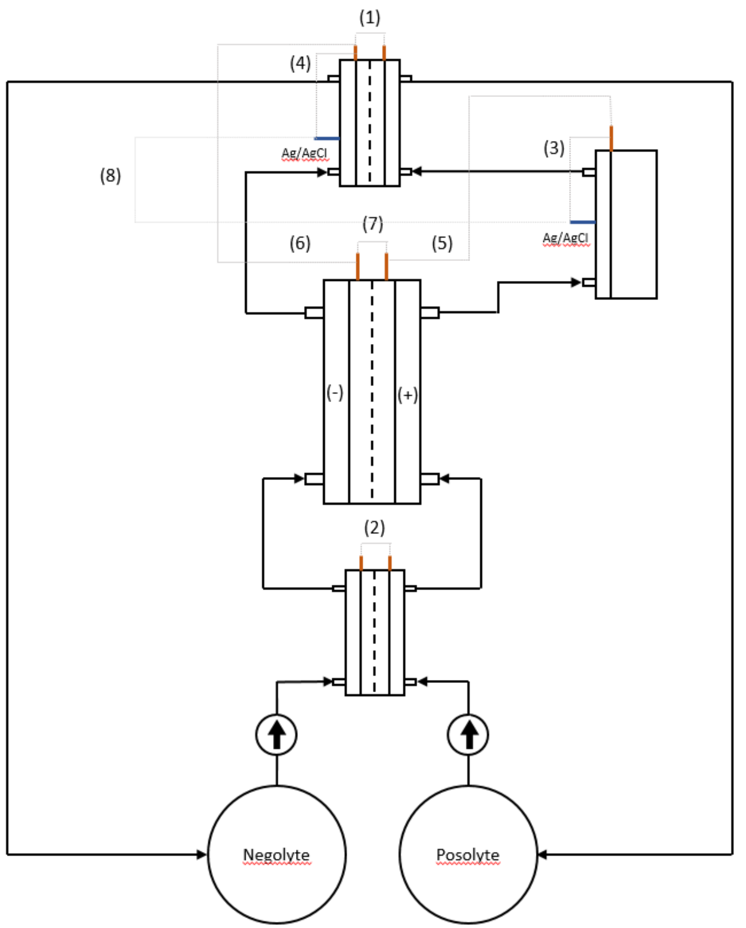
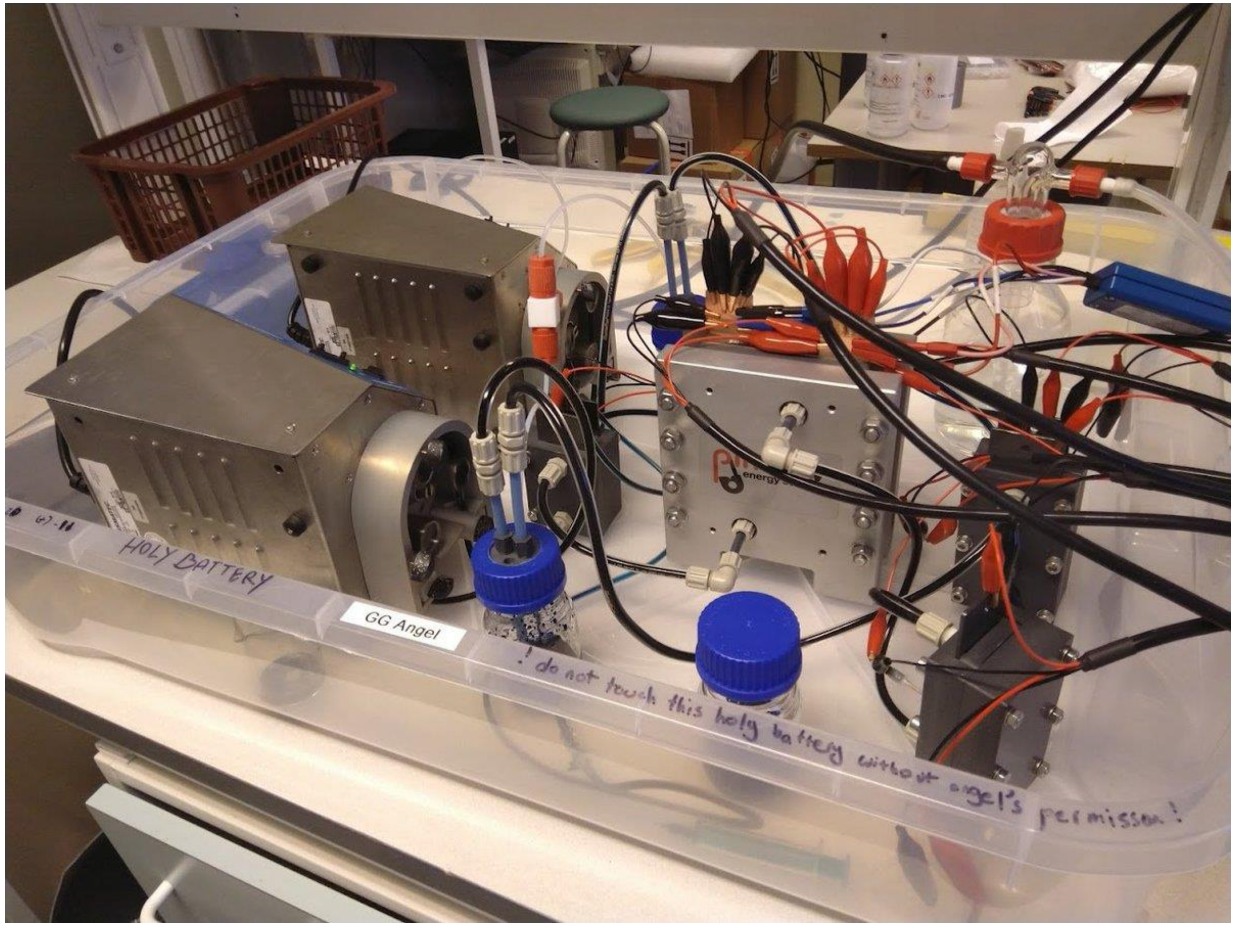
Gabriel Gonzalez
University of Turku

Test bench for flow batteries





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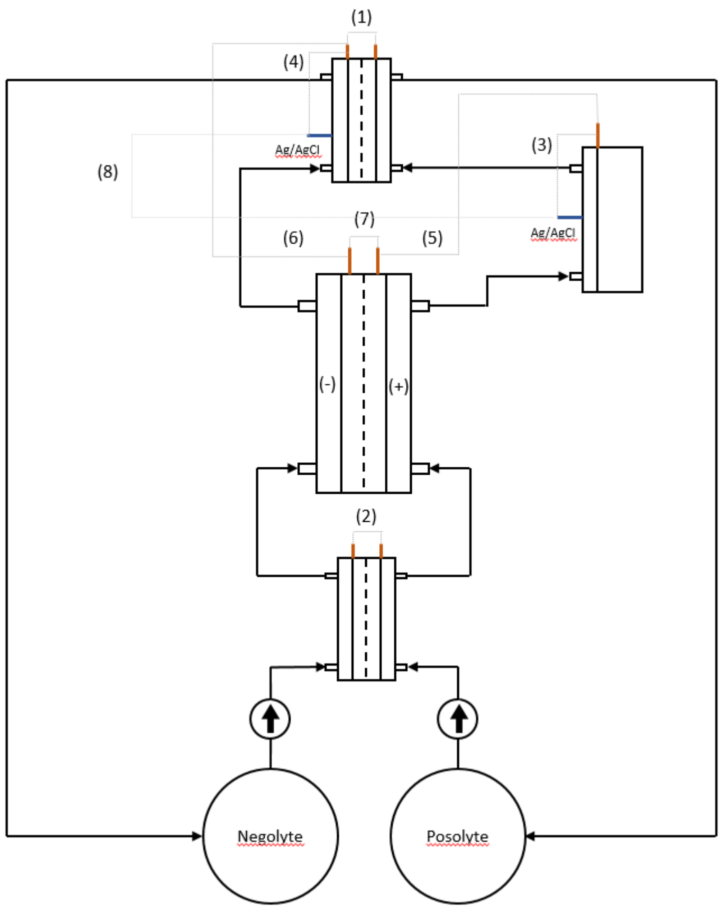

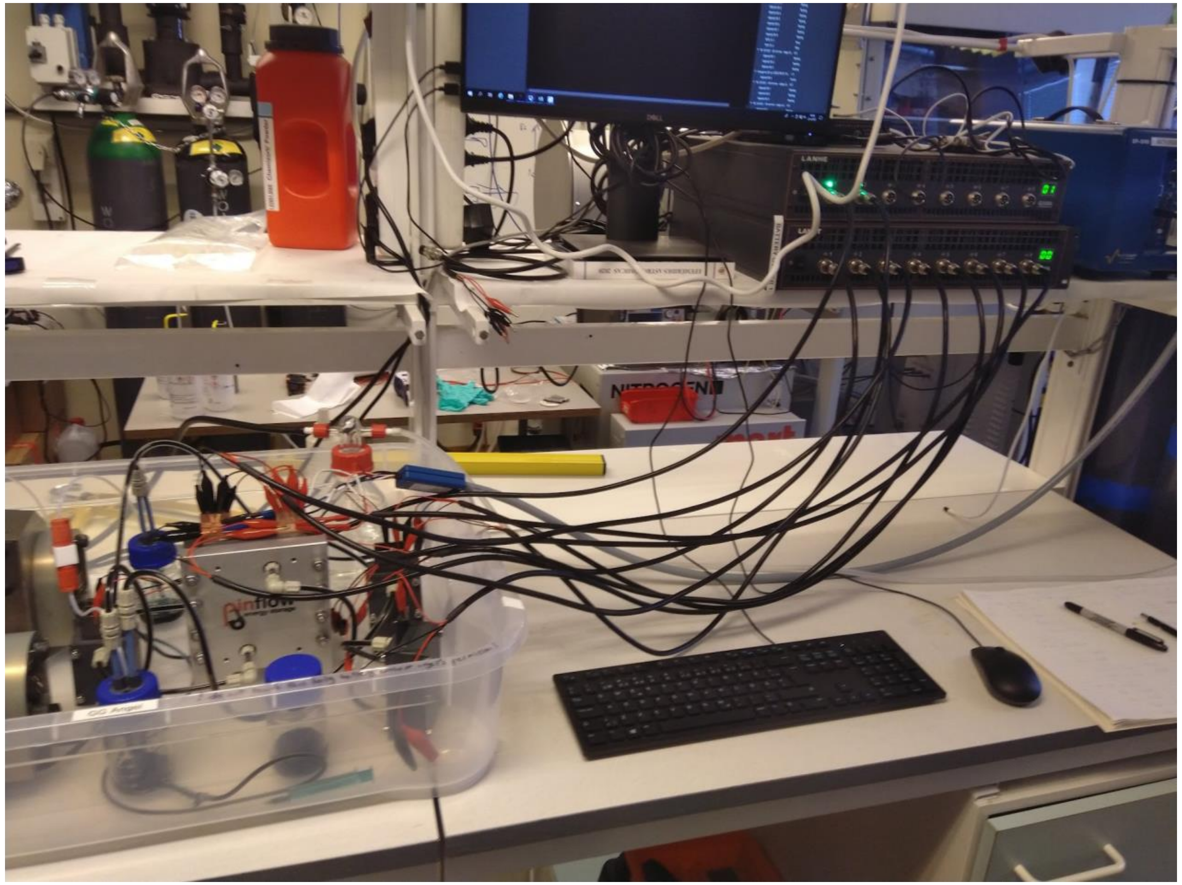

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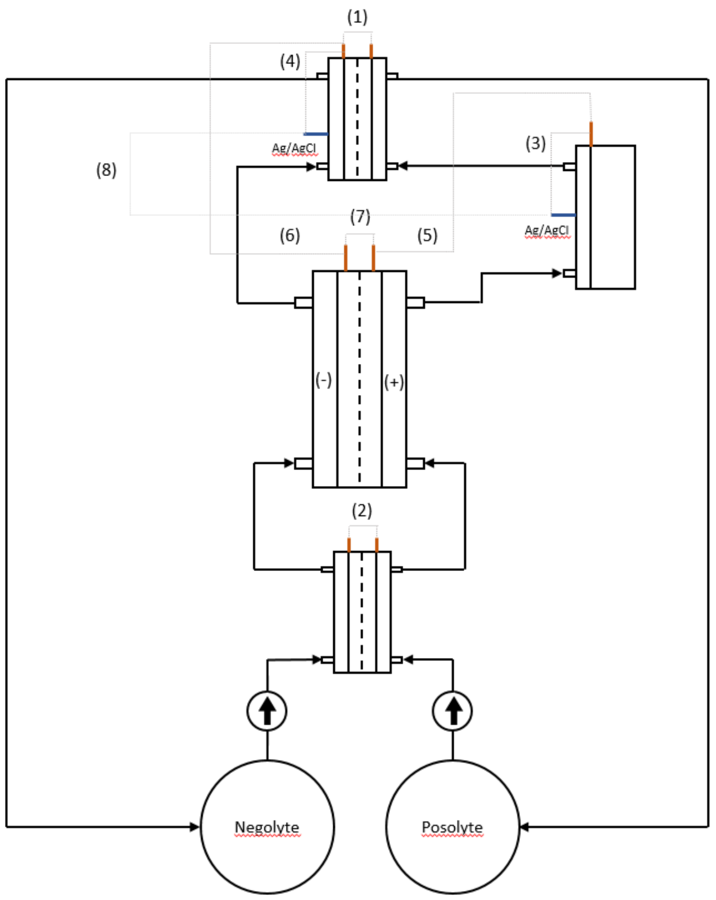
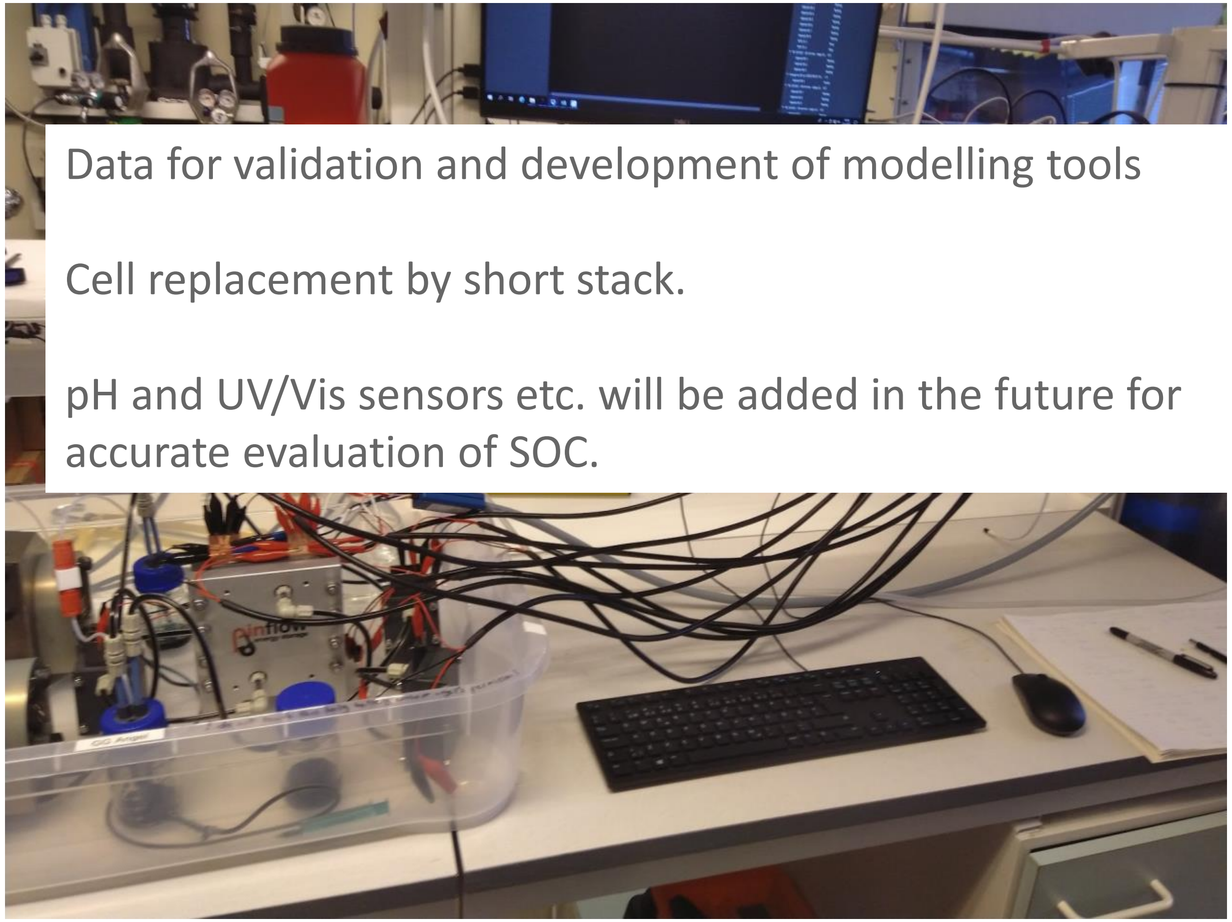
Test bench for flow batteries

Gabriel Gonzalez
University of Turku





Data for validation and development of modelling tools

Cell replacement by short stack.

pH and UV/Vis sensors etc. will be added in the future for accurate evaluation of SOC.

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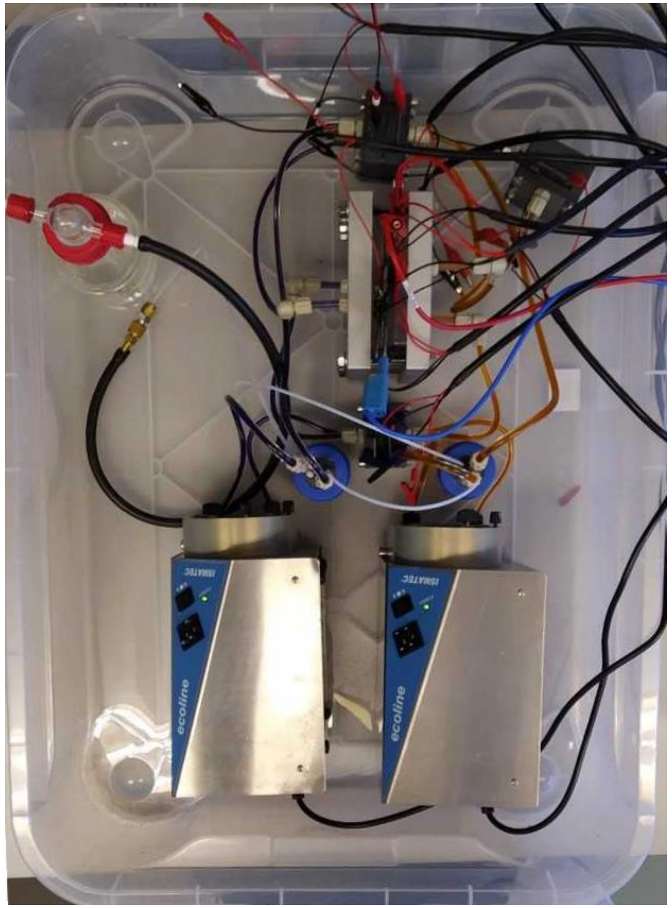
Flow battery testing

- Advantages of the set-up
  - 8 potentials measured at once vs. 1 typically measured
  - Better understanding of the behaviour of the system
  - Produces data to compare the values in simulations
  - More accurate evaluation of different parameters in simulations



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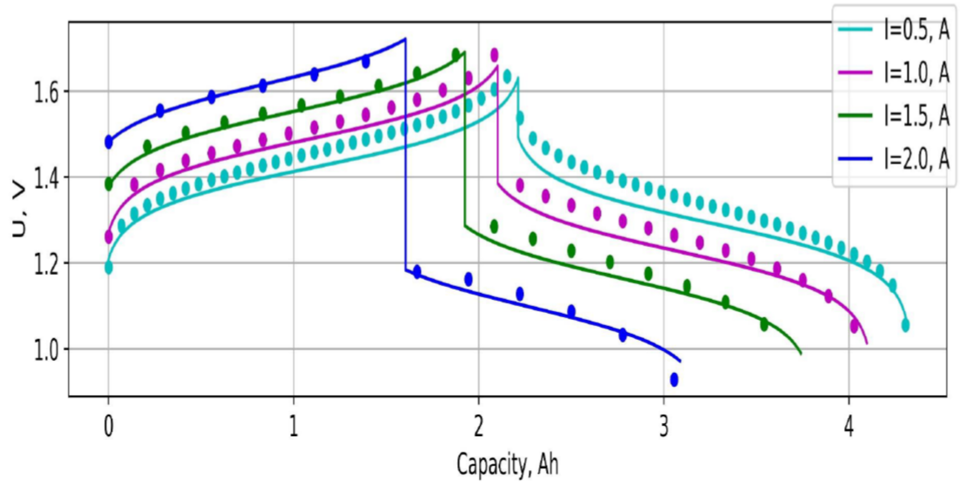
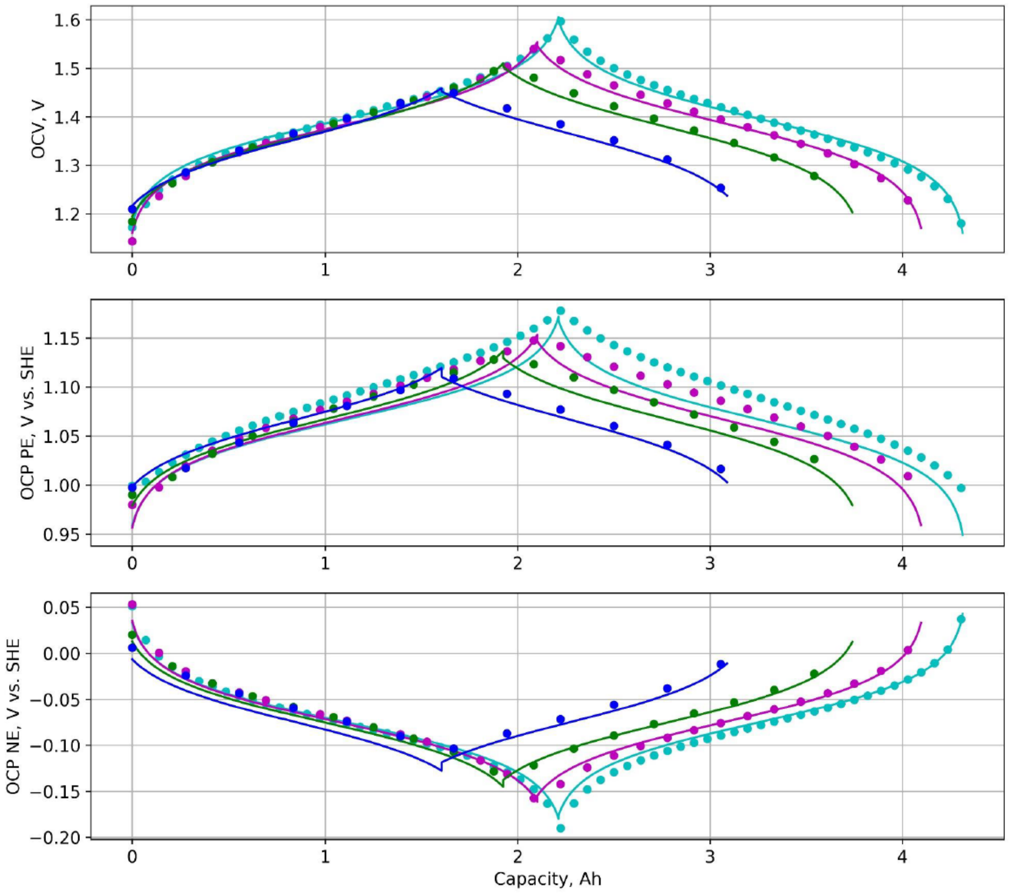
Model validation



Losses model: Ohmic, U_0^* = 1.367 V
Mean error: ~4%



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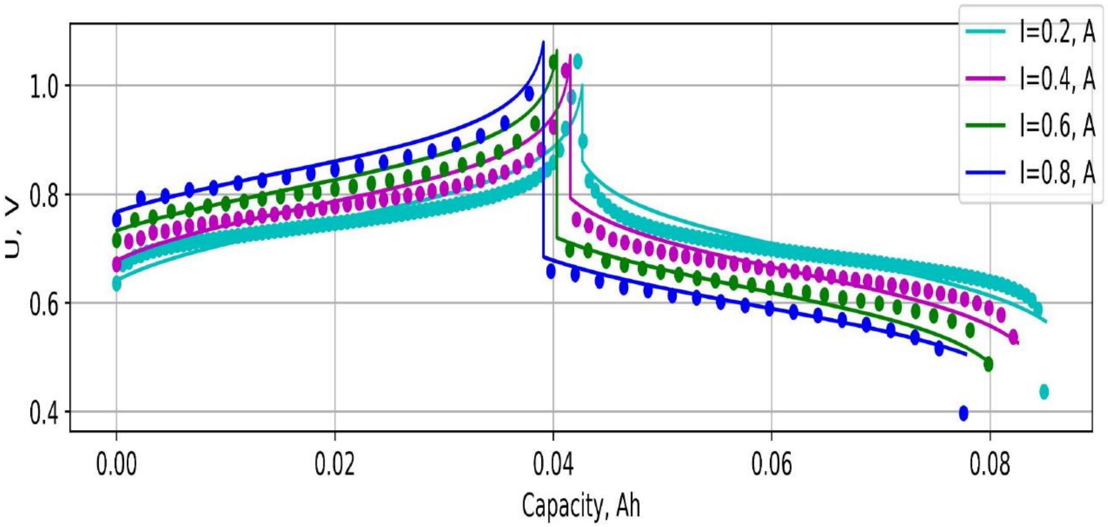
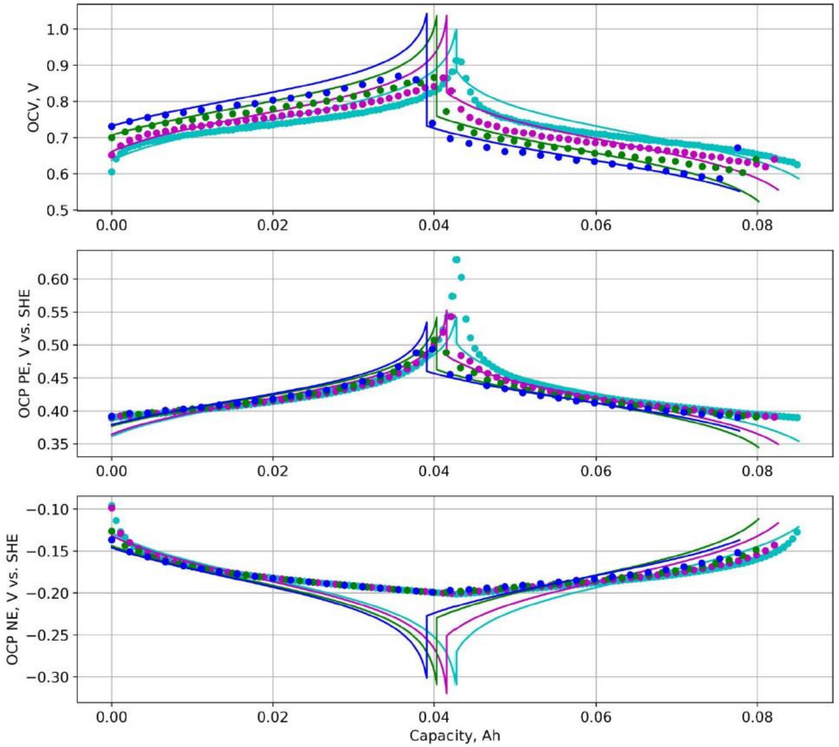
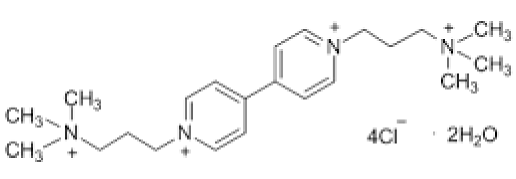
Model validation

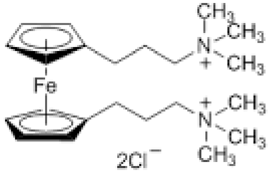




Losses model: Ohmic+conc, U_0^* = 0.720 V
Mean error: ~9%



BTMAP-Vi Dihydrate



BTMAP-Fc

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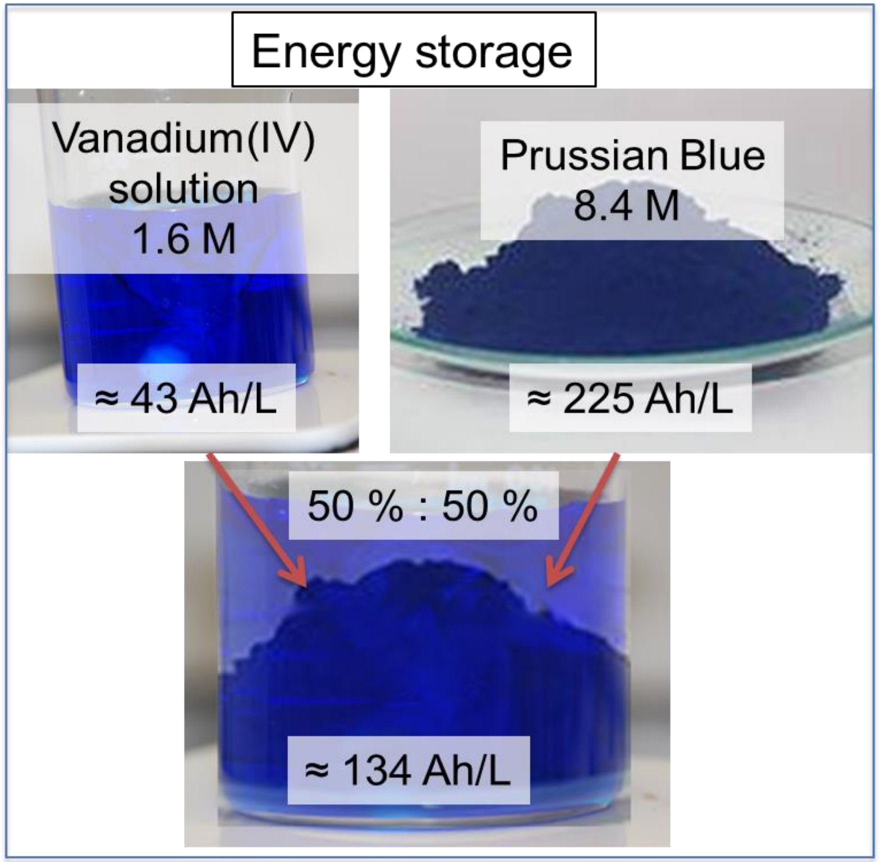
Next Generation Batteries with solid boosters



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Solid boosters

Solid boosters

Ferro/ferricyanide coupled with Prussian blue

Data for modelling

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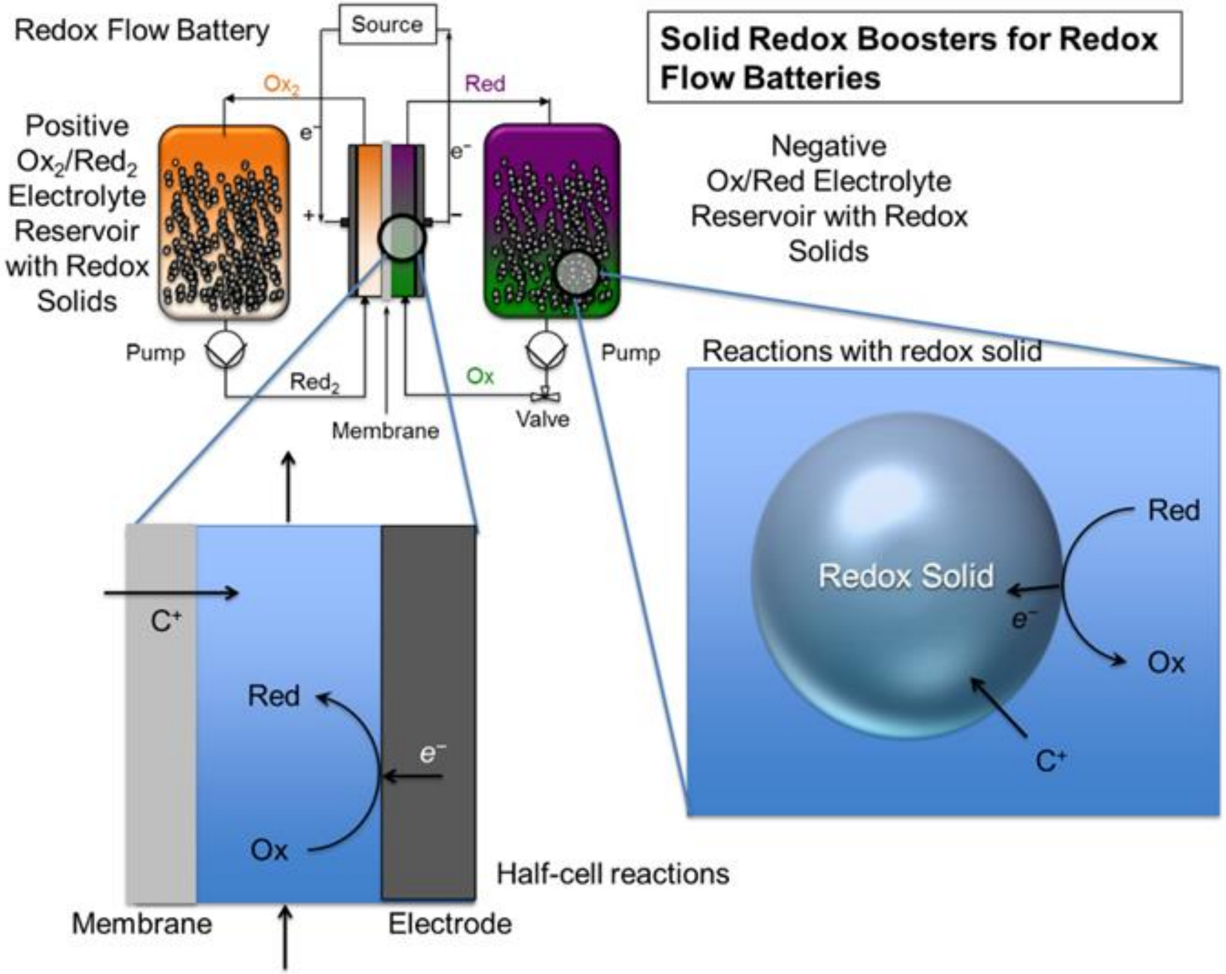
The concept of solid boosters and molecular wiring



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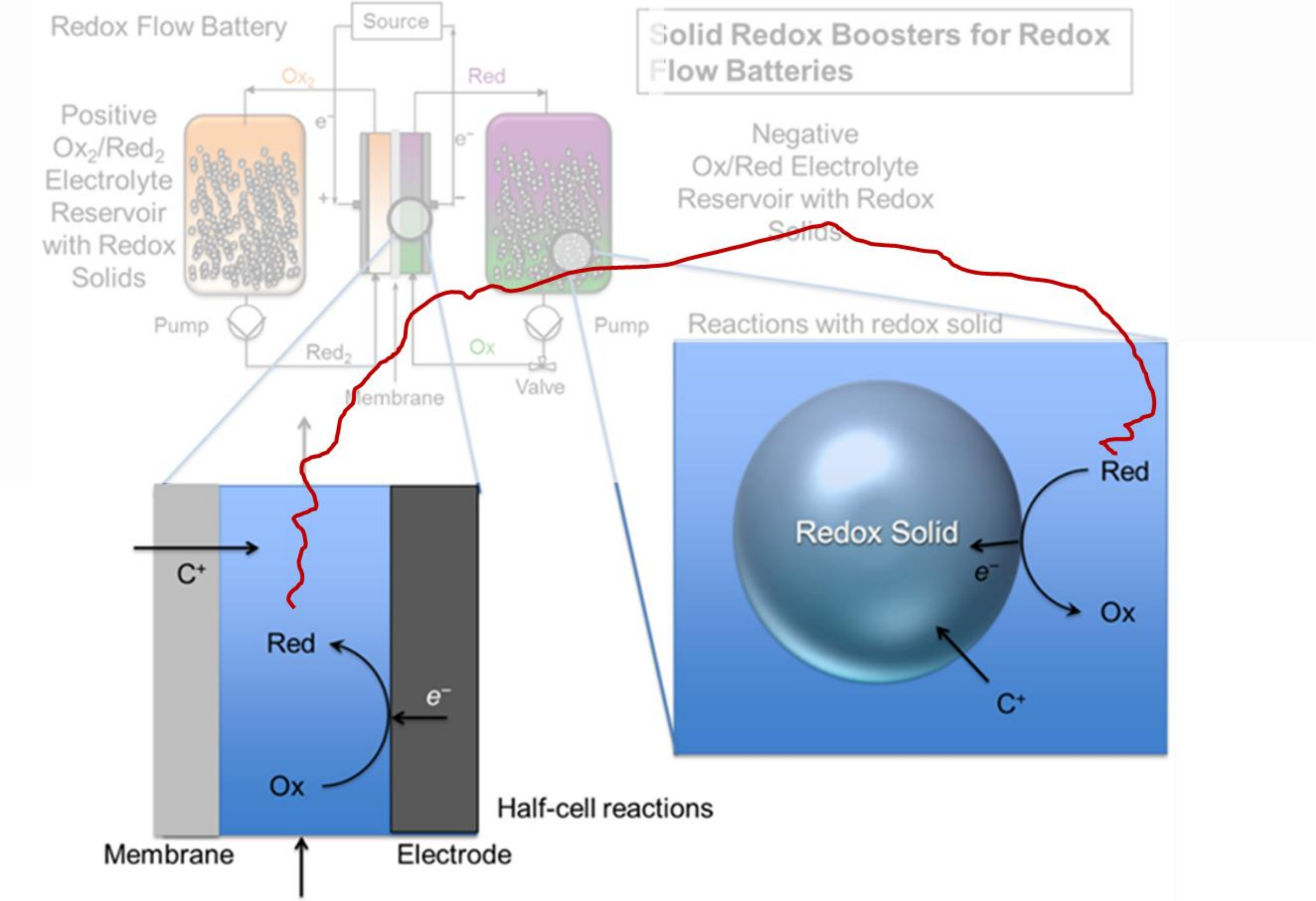
The concept of solid boosters and molecular wiring



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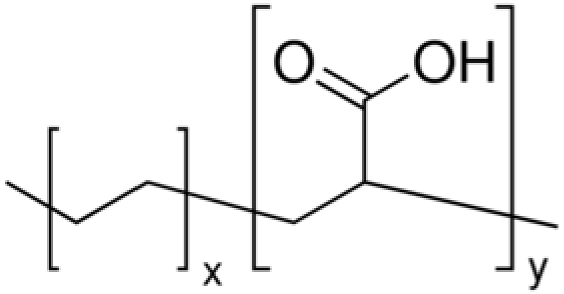
Comparing different booster recipes

Starting point

80% Redox solid: Prussian White $K_2Fe^{II}Fe^{III}(CN)_6$
10% Conductive additive: Carbon Black (Super P)
10% Binder: PEAA (poly(ethylene-co-acrylic acid))
Solvent: Tetrahydrofuran (THF)



PEAA

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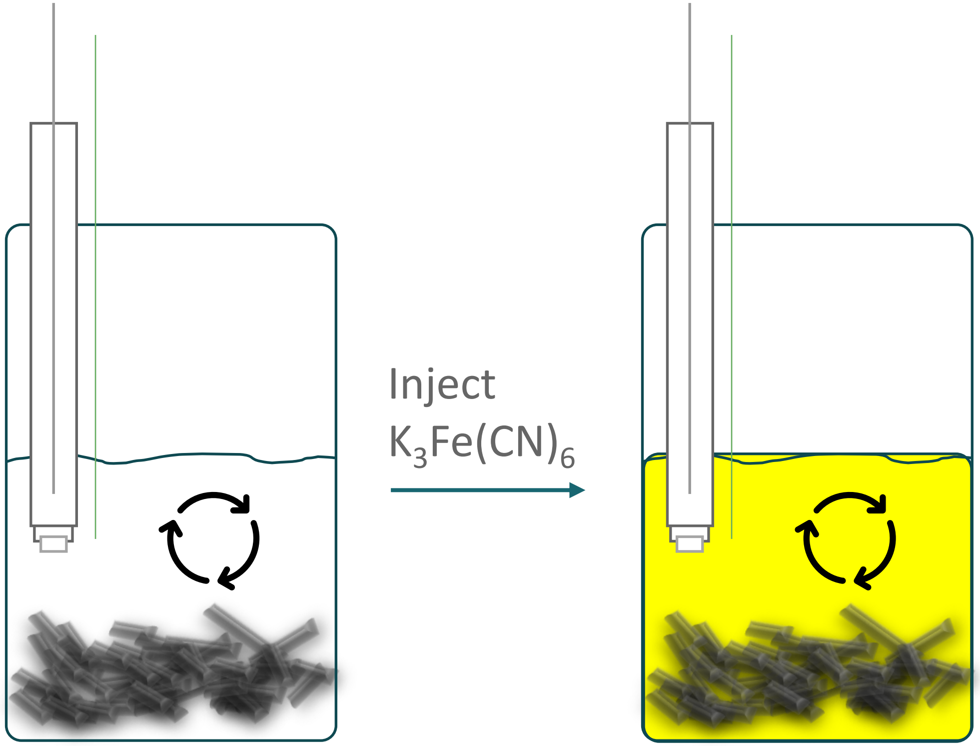
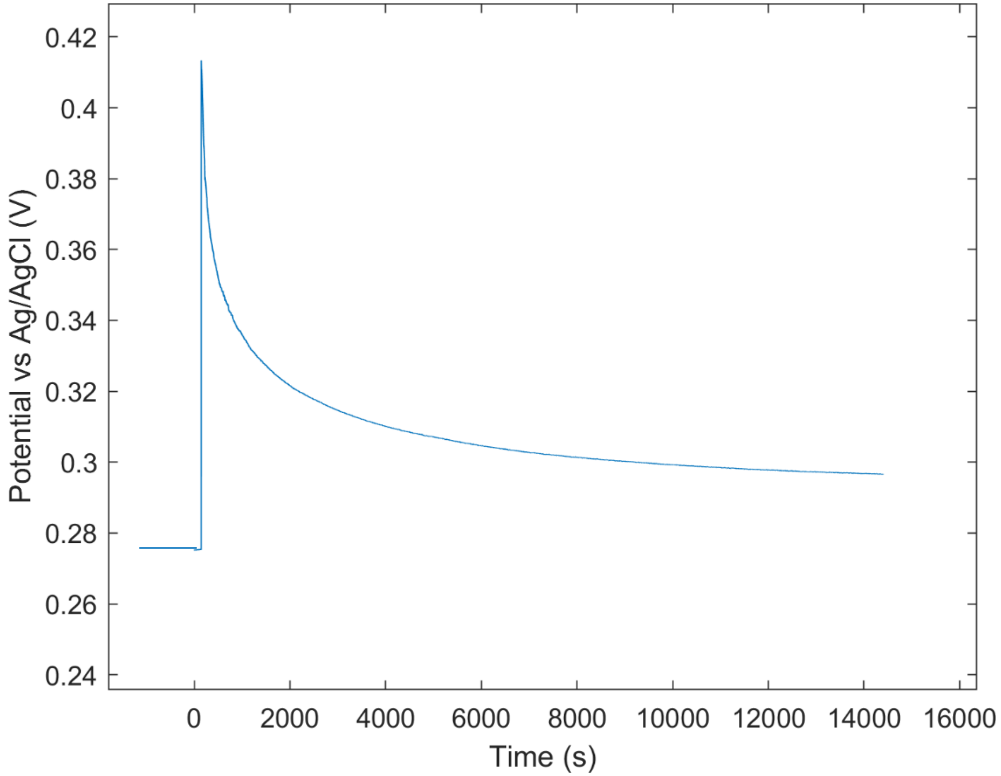
Initial testing





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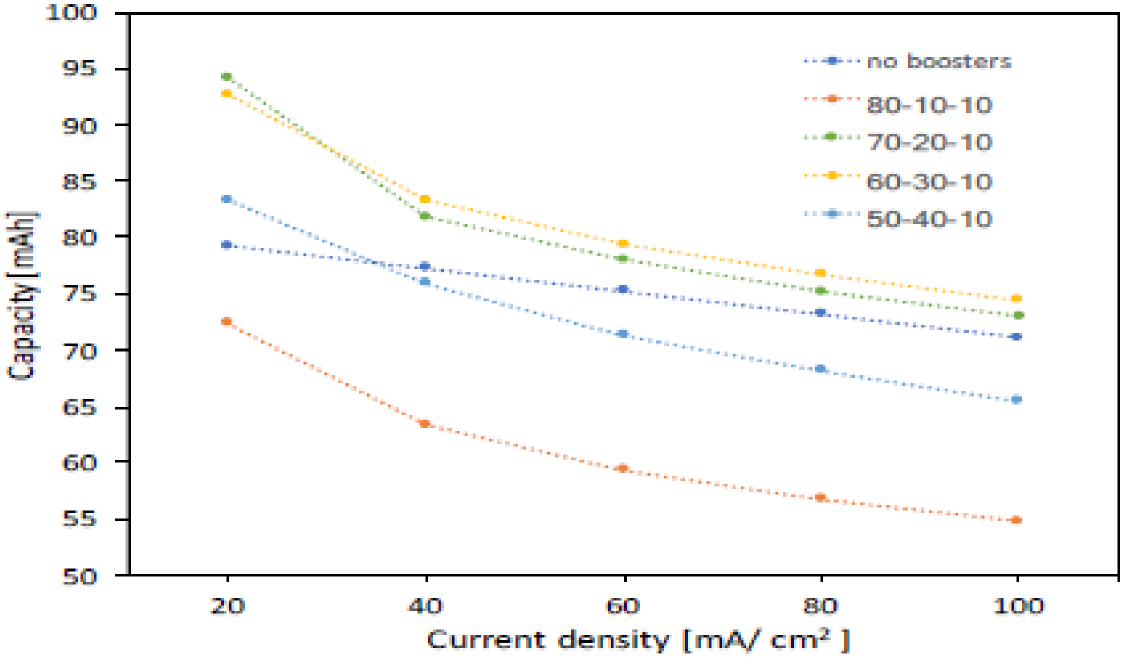
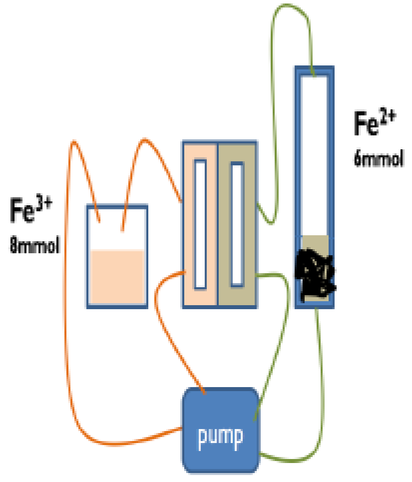
Optimizing the booster composition

Active material – carbon – binder ratios





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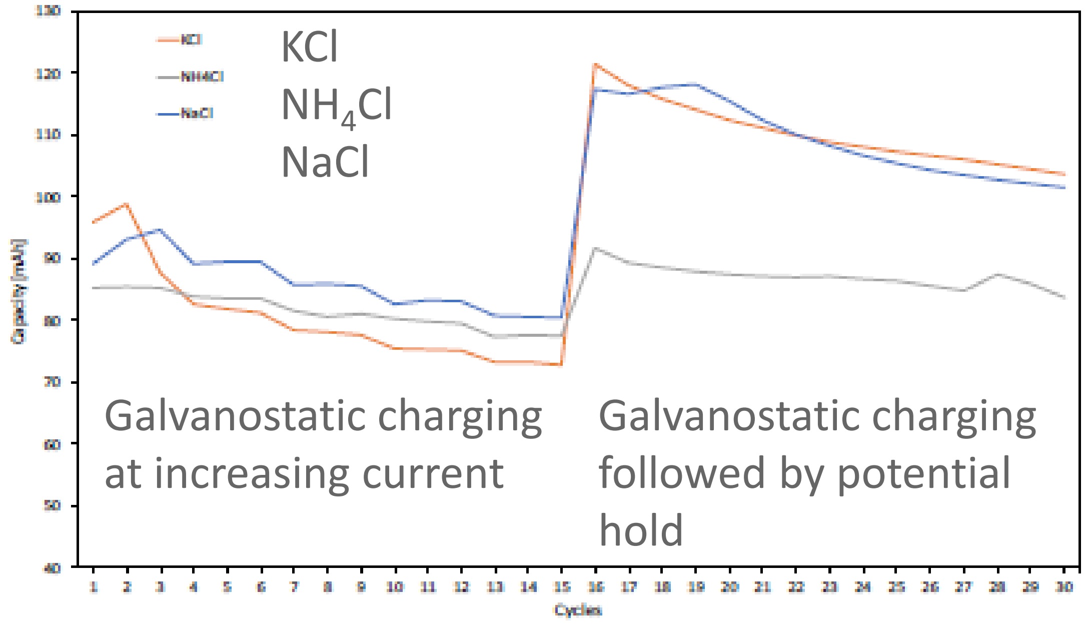
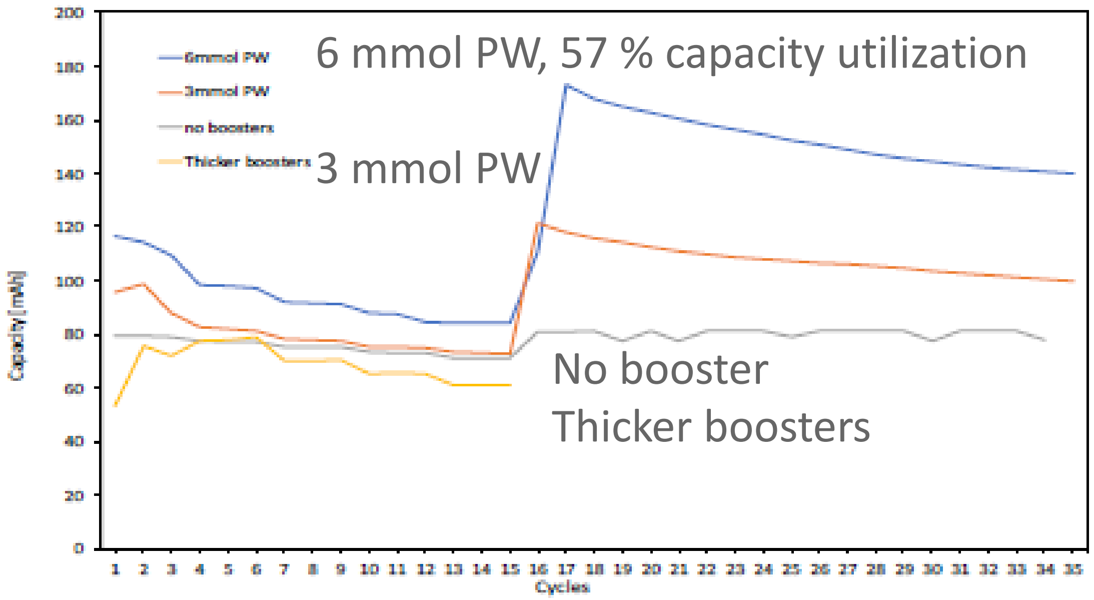
System optimization





Conclusions

- Excellent experimental set-up to generate data for verification of simulations
- Test bench for model verification developed
  - Compatible with short-stack
- Experimental set-up to measure kinetics of charging and dischargin of solid boosters developed

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Questions & Answers

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Thank you!

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