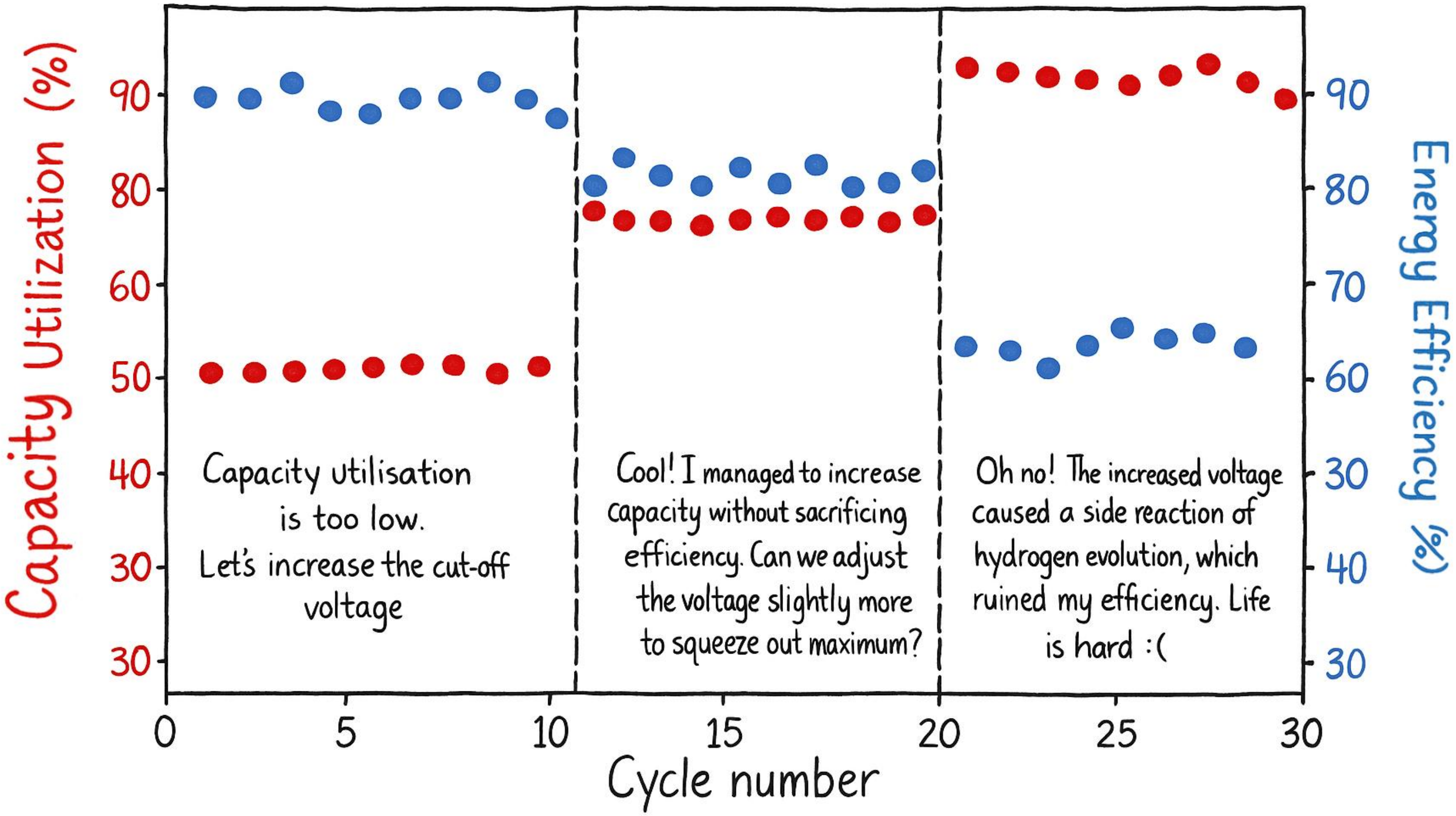
ALL-IRON FLOW BATTERY COUPLED WITH ROOM TEMPERATURE HYDROGEN PRODUCTION

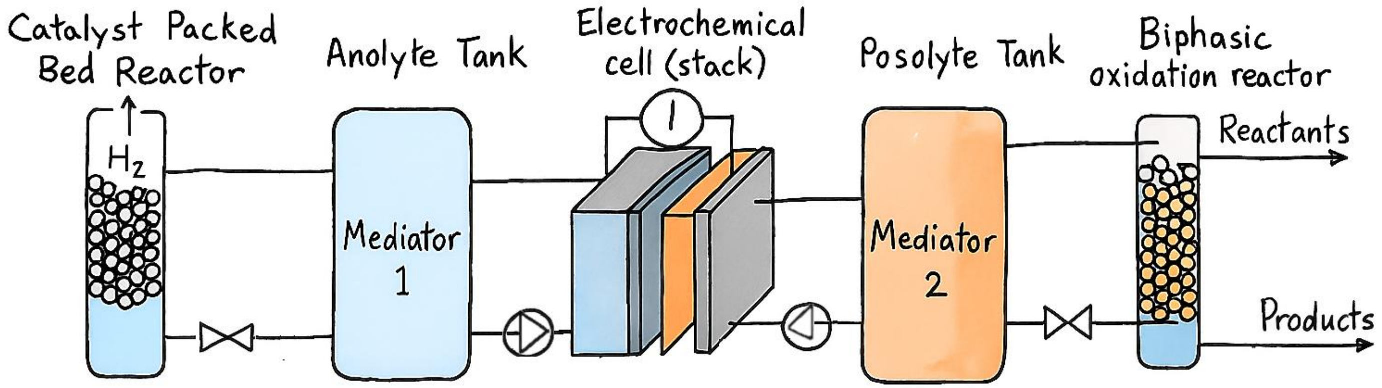
MIKHAIL PETROV, POSTDOC
AARHUS UNIVERSITY, DEPARTMENT OF BIOLOGICAL AND CHEMICAL ENGINEERING

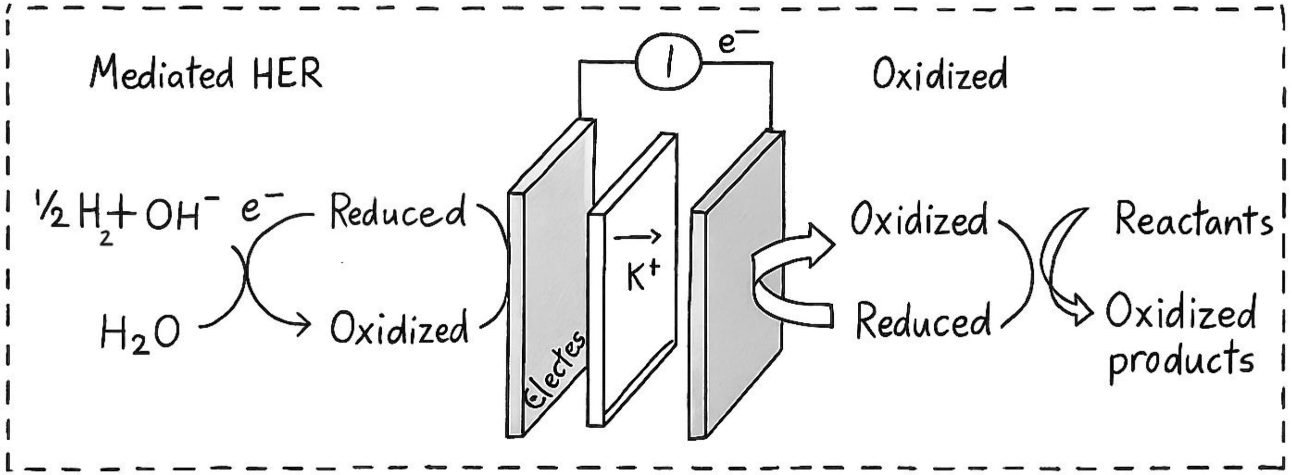
HYDROGEN? FOR THE SAKE OF WHAT?



Hydrogen evolution is regarded as an undesirable and adverse reaction to be avoided in flow batteries.
However … **it is possible to take advantage of it**

DUAL FLOW CONCEPT



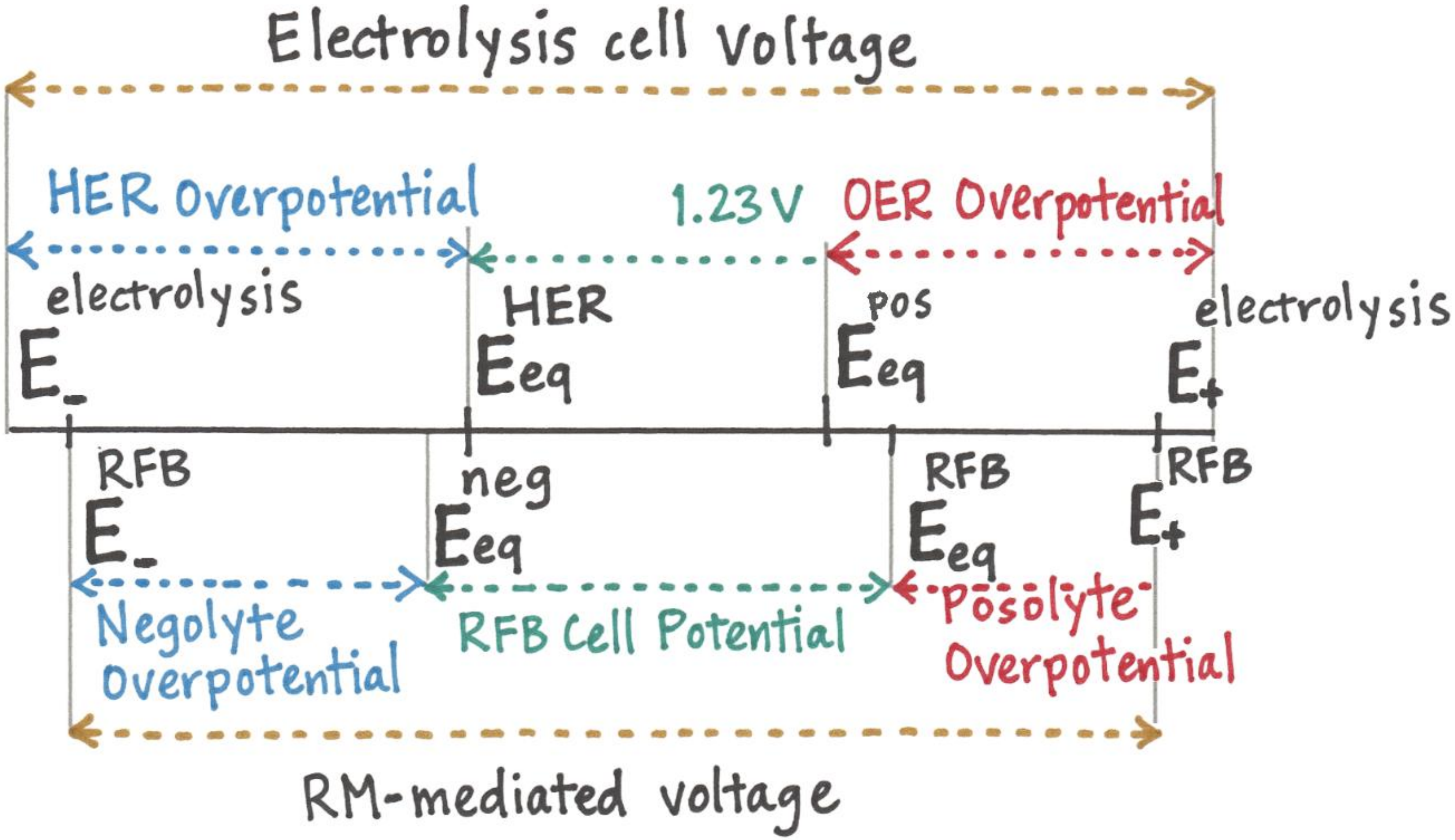


In the dual flow approach, we **aim to run HER/OER in separate reactors** filled **with catalytic materials** that can deplete pre-charge electrolytes through corresponding chemical reactions.

By controlling the valves, we **can switch the system between** a basic energy storage mode and a mixed mode that incorporates H_2/O_2 production.

AARHUS UNIVERSITY

ADVANTAGES OF DUAL FLOW



vs Flow Batteries

- Enhanced capacity
- Can adjust to the pace of renewable energy by switching between energy storage and H_2 production

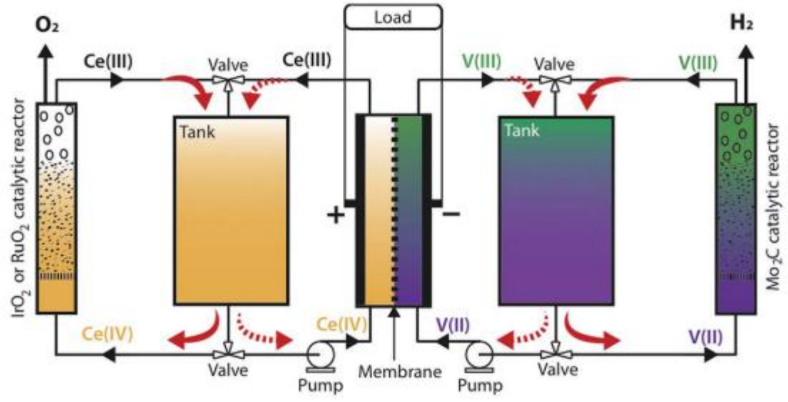
vs Electrolysis

- Spatially decoupled HER and OER
- Lower cell voltages

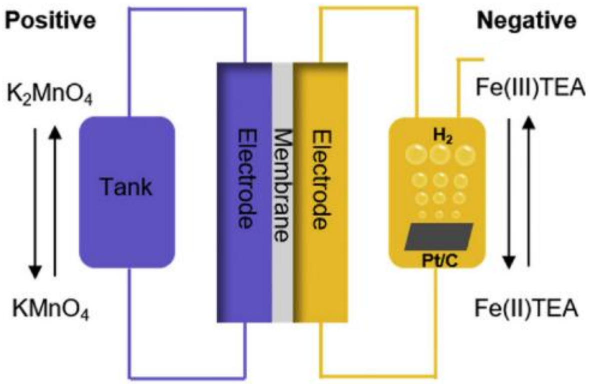
Unique

- Other electrosynthetic reactions are available to couple

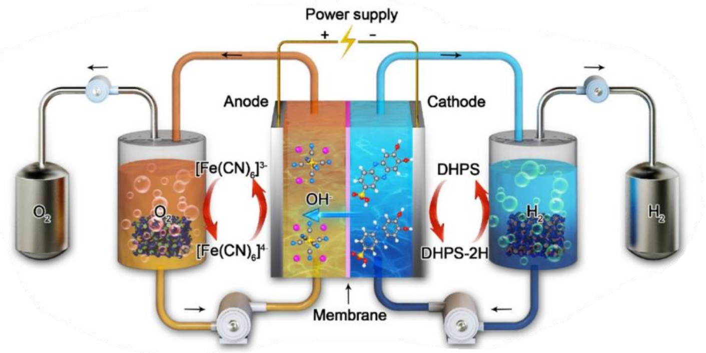
OBJECTIVES



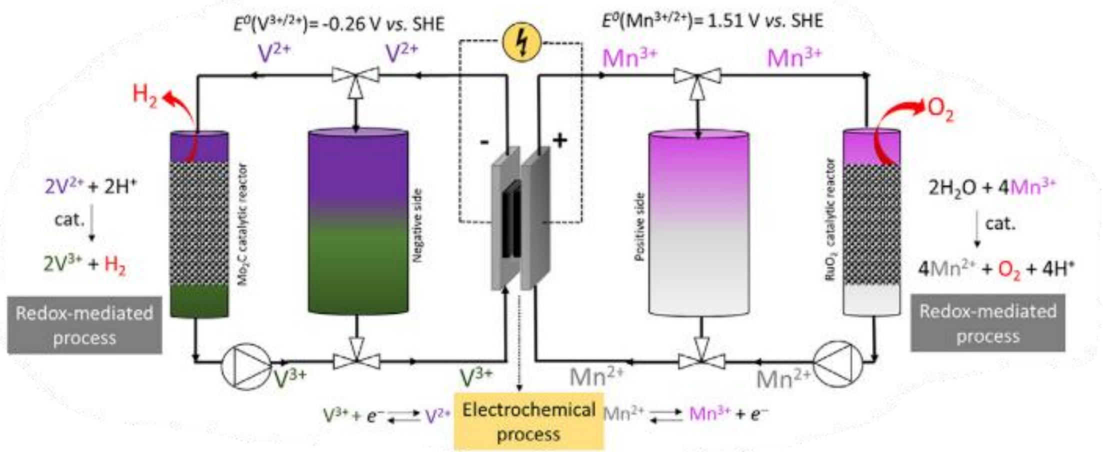
Amstutz, V. et al, (2014). Energy and Environmental Science



Ji, Y. et al (2020) . Int. Journal of Hydrogen Energy



Zhang, F. et al (2021). JACS



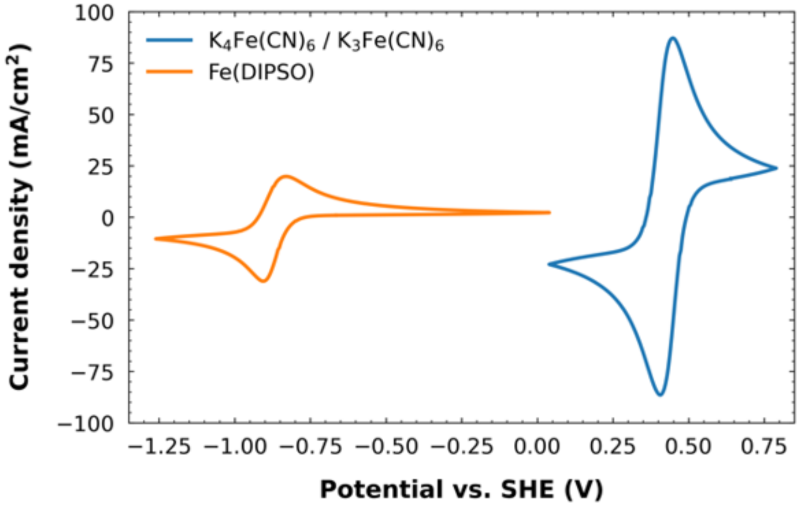
Reynard, D. Et al (2021). Cell Reports Physical Science

Unlike most previous works, we focus on **alkaline conditions** (easier to find RM for the positive side) and **redox mediators with potentials near HER/OER**.

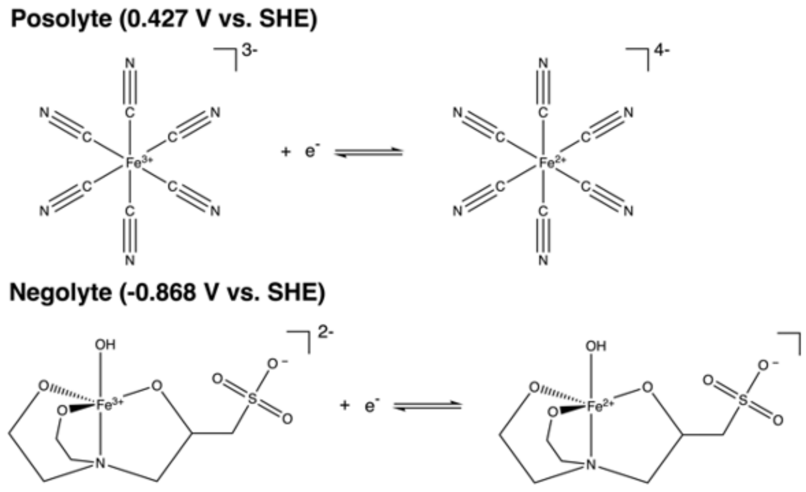
BACKBONE

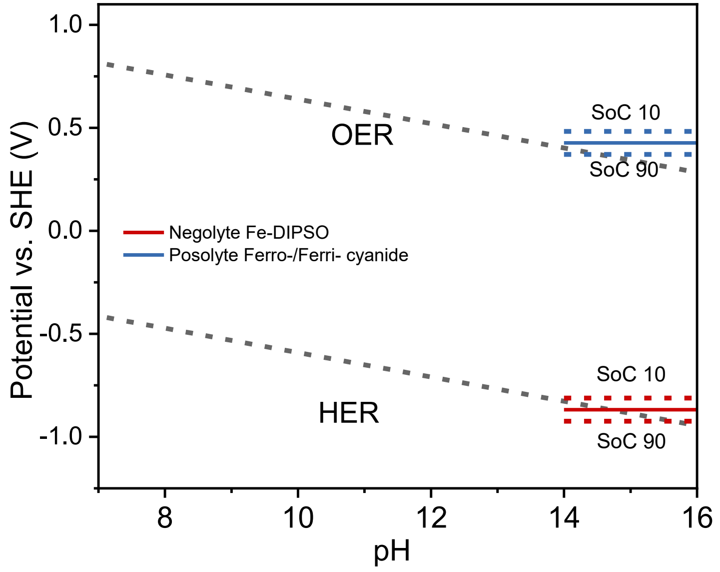
FLOW BATTERY AND MEDIATORS

REDOX MEDIATORS



0.2 M Fe-DIPSO in 4 M KOH and 0.25 M $K_4Fe(CN)_6$ / 0.25 M K_3 $Fe(CN)_6$ in 1 M KOH, 100 mVs

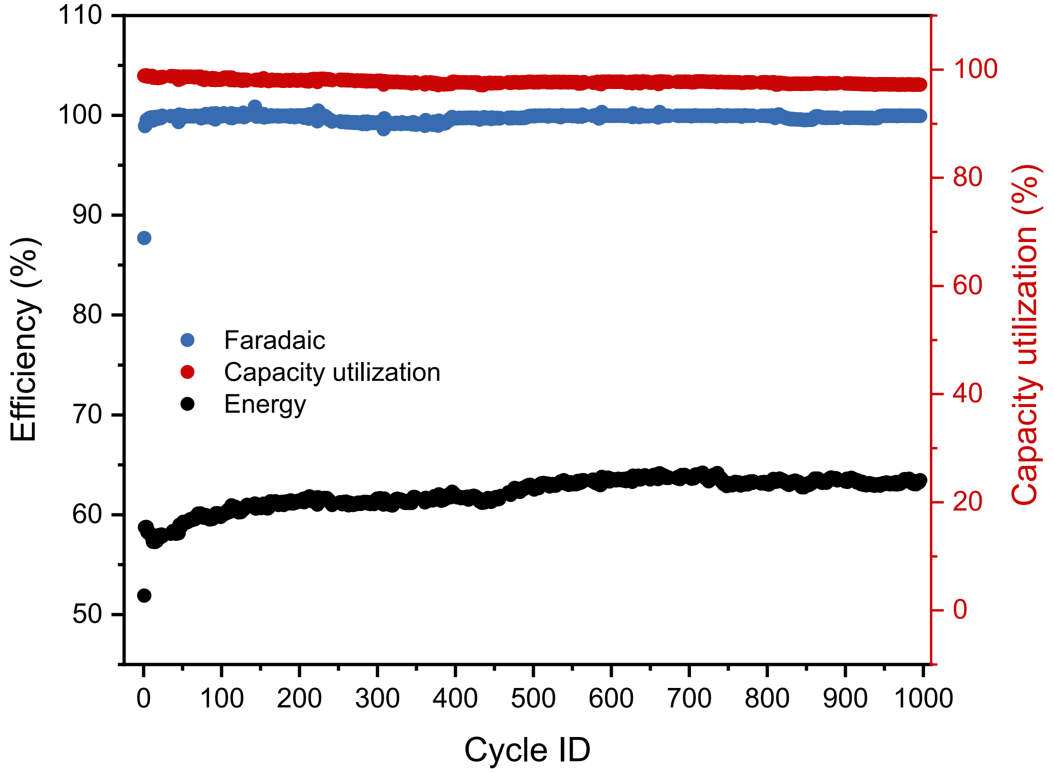




From a thermodynamic perspective, these **iron-based electrolytes are capable of mediating** HER/OER.

FLOW BATTERY CYCLING

Although the energy efficiency (EE) is fairly low (around 60%), the **capacity fade rate is simply excellent** (less than 0.01% per day), which is likely a crucial parameter in the context of a dual flow battery

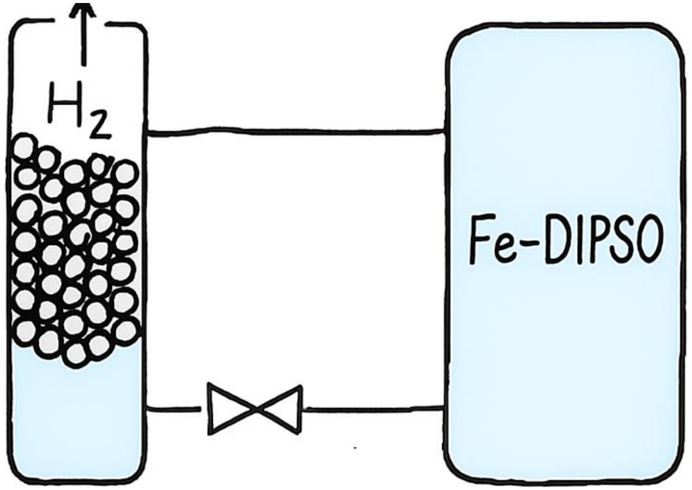


Negolyte – 50 mL of 0.2 M Fe-DIPSO @ 4M NaOH, Posolyte – 50 mL of 0.2 M $K_4[Fe(CN)_6]$ @ 4M NaOH. Membrane: anion exchange FAAM-20. 25 cm^2 active area. CCCV cycling between 0.75 and 1.5 V. Current density of 50 mA cm^{-2}. Cut-off current density is 3 mA cm^{-2} and 2 mA cm^{-2} for the charge and discharge, respectively

CORE

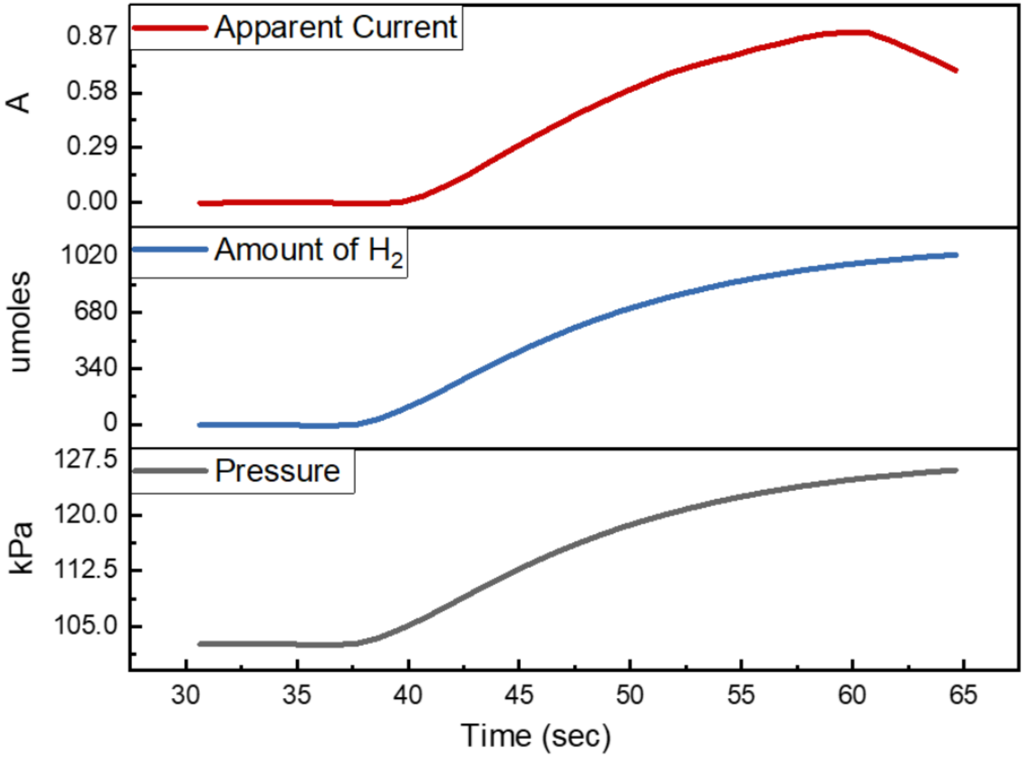
MEDIATED HER AND OER

FE-DIPSO DO CARRY OUT HER



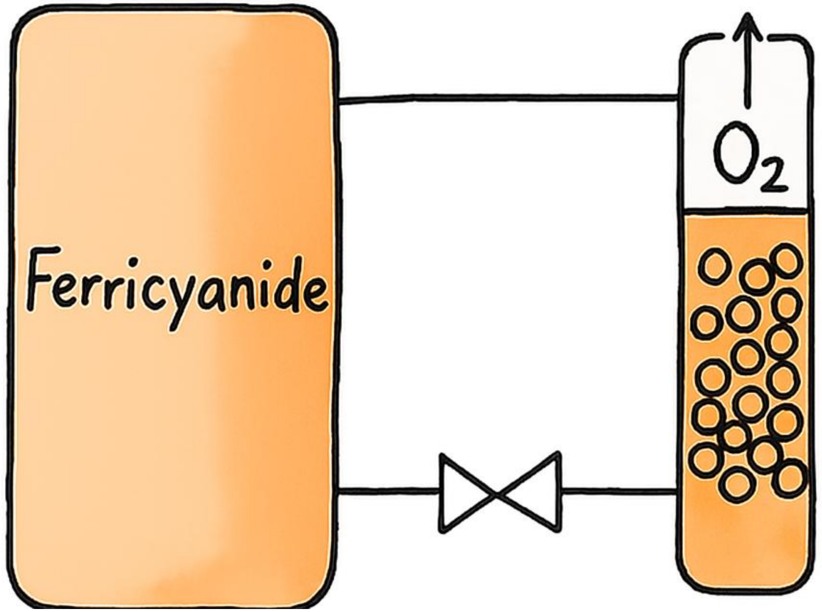
25 mL of reduced 0.2 M Fe-DIPSO @ 4M NaOH added to 0.076 g Raney Nickel in a 30 mL bottle

Current that the reactor theoretically sustain, when connected to an electrochemical cell

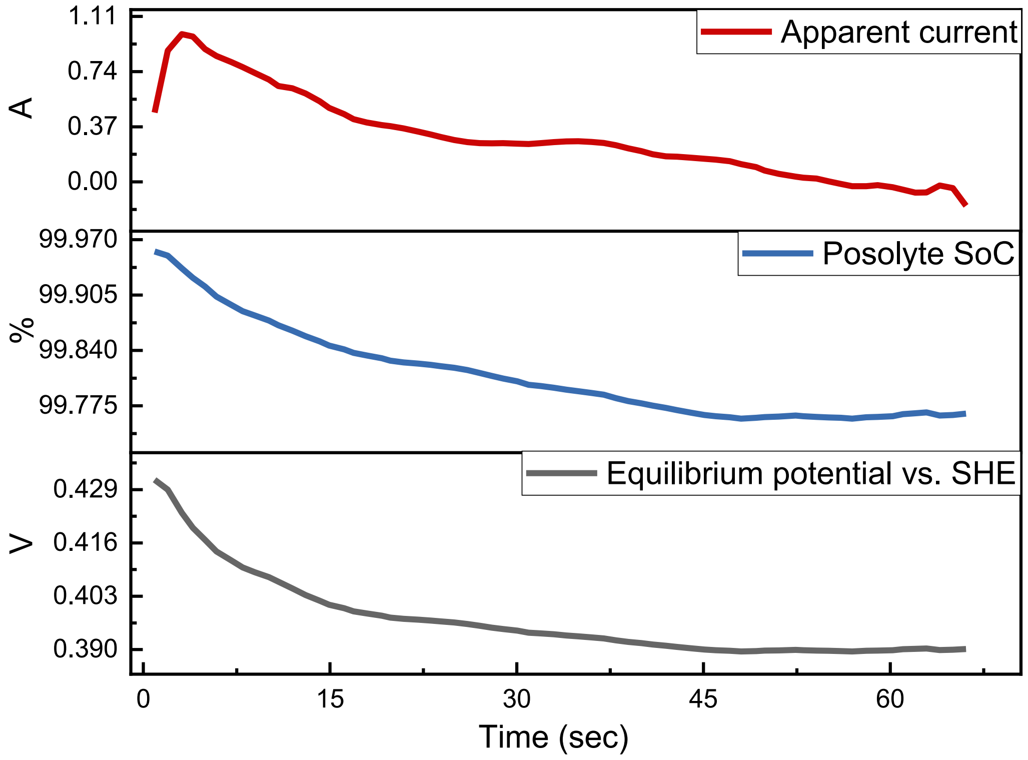


HER is tracked through pressure changes after mixing charged negolyte and a catalyst

FERRICYANIDE DO CARRY OUT OER



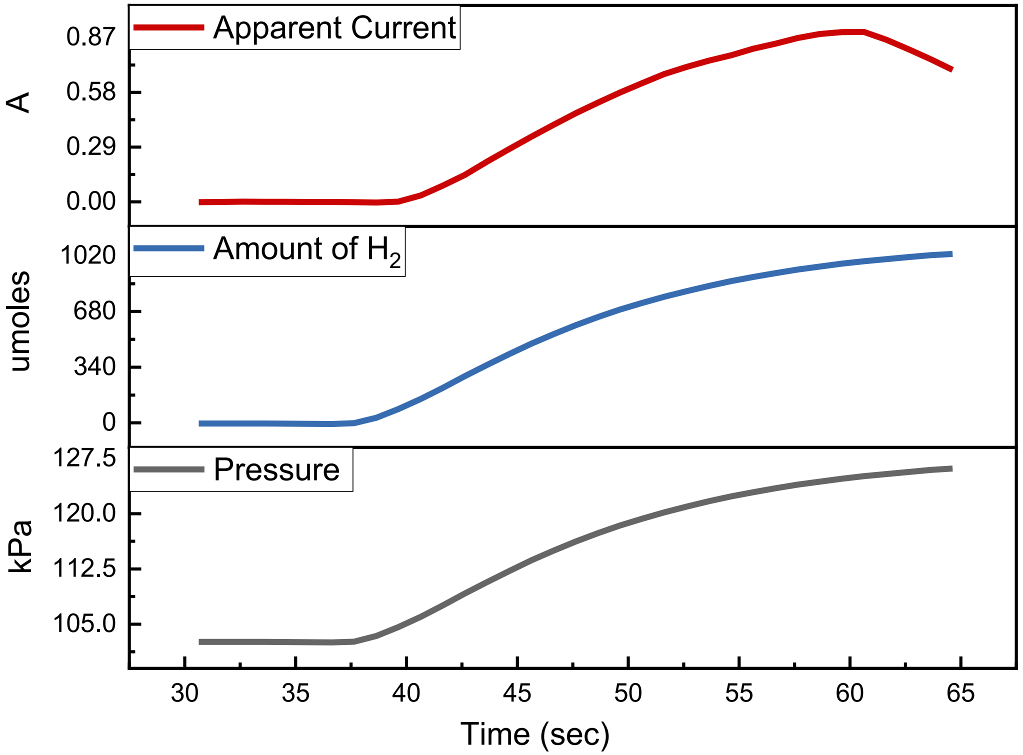
100 mL of reduced 0.5 M potassium ferricyanide @ 4M NaOH added to 1.0 g Raney Nickel in a 115 mL bottle



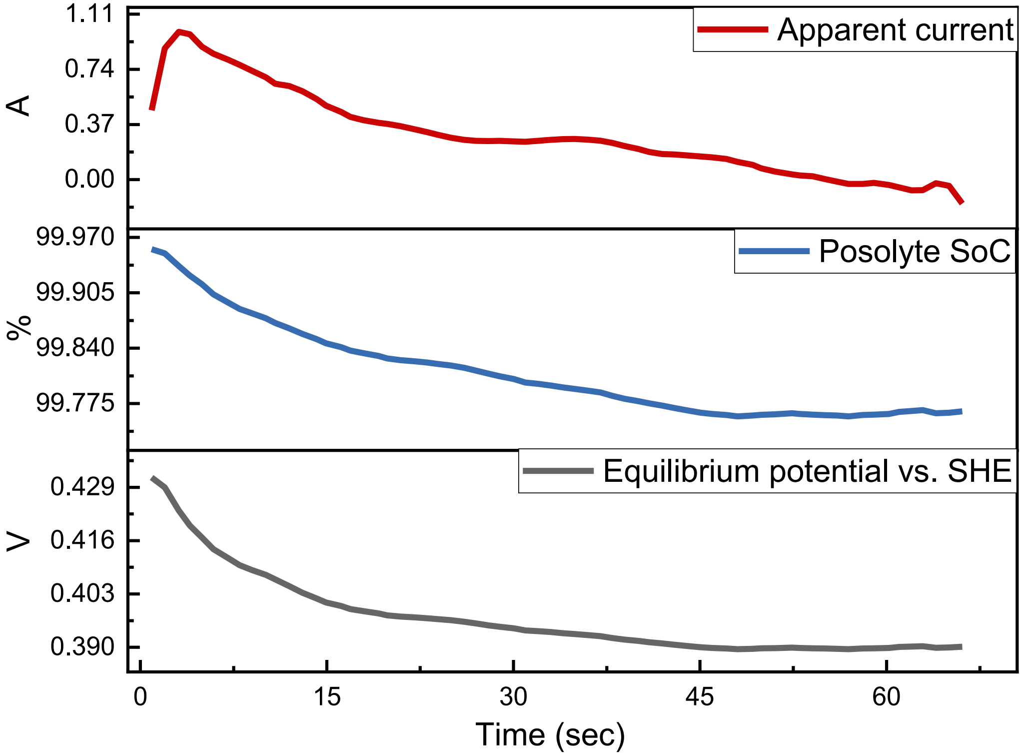
OER is tracked through equilibrium potential changes

MEDIATORS ARE IN ALIGNMENT

Hydrogen evolution (HER)



Oxygen evolution (OER)



Reactors can sustain **up to 1A of current**
Estimated with a water displacement method**, Faradaic Efficiency** was about 95-99 %

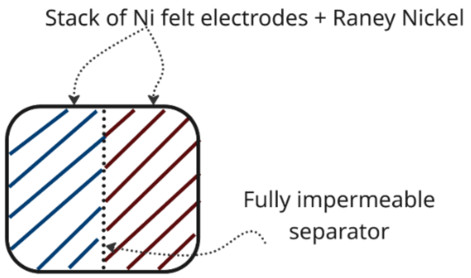
ALL TOGETHER

PERFORMANCE OF A HYBRID SYSTEM

SETUP USED

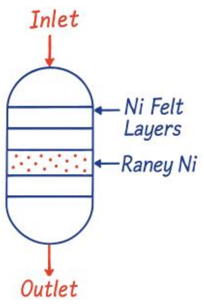
Two modes of operation:
- Valves closed and reactors off: Just Flow Battery
- Valves open and reactors on: Dual flow battery carrying out spatially decoupled electrolysis (when charging)

Two types of reactors are used
- Flow “electrochemical” cell with split chambers
- Fixed bed reactor

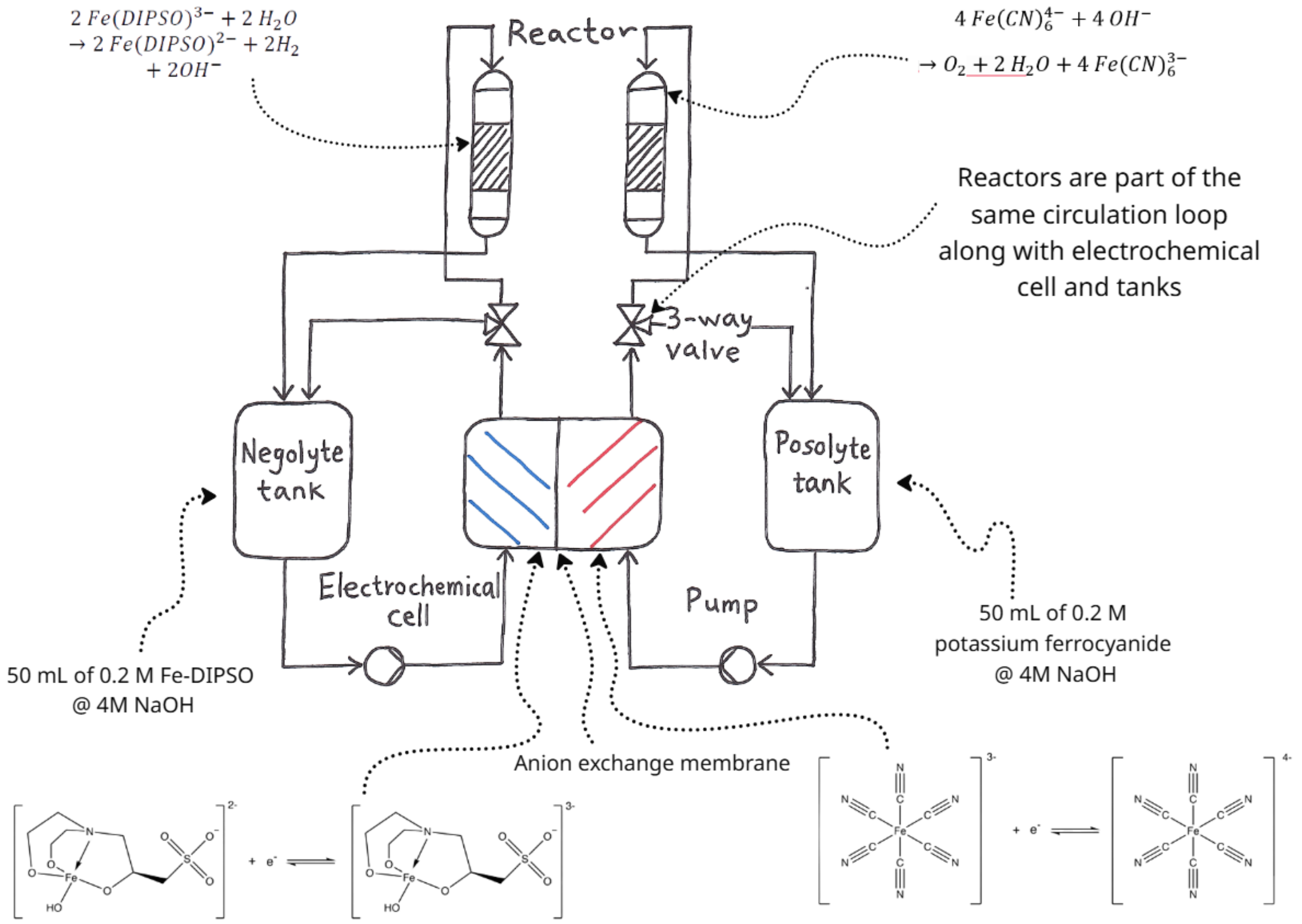

Stack of Ni felt electrodes + Raney Nickel

Fully impermeable separator

ELECTROCHEMICAL REACTOR



PACKED BED REACTOR



$2\,Fe(DIPSO)^{3-} + 2\,H_2O \rightarrow 2\,Fe(DIPSO)^{2-} + 2H_2 + 2OH^-$

$4\,Fe(CN)_6^{4-} + 4\,OH^- \rightarrow O_2 + 2\,H_2O + 4\,Fe(CN)_6^{3-}$

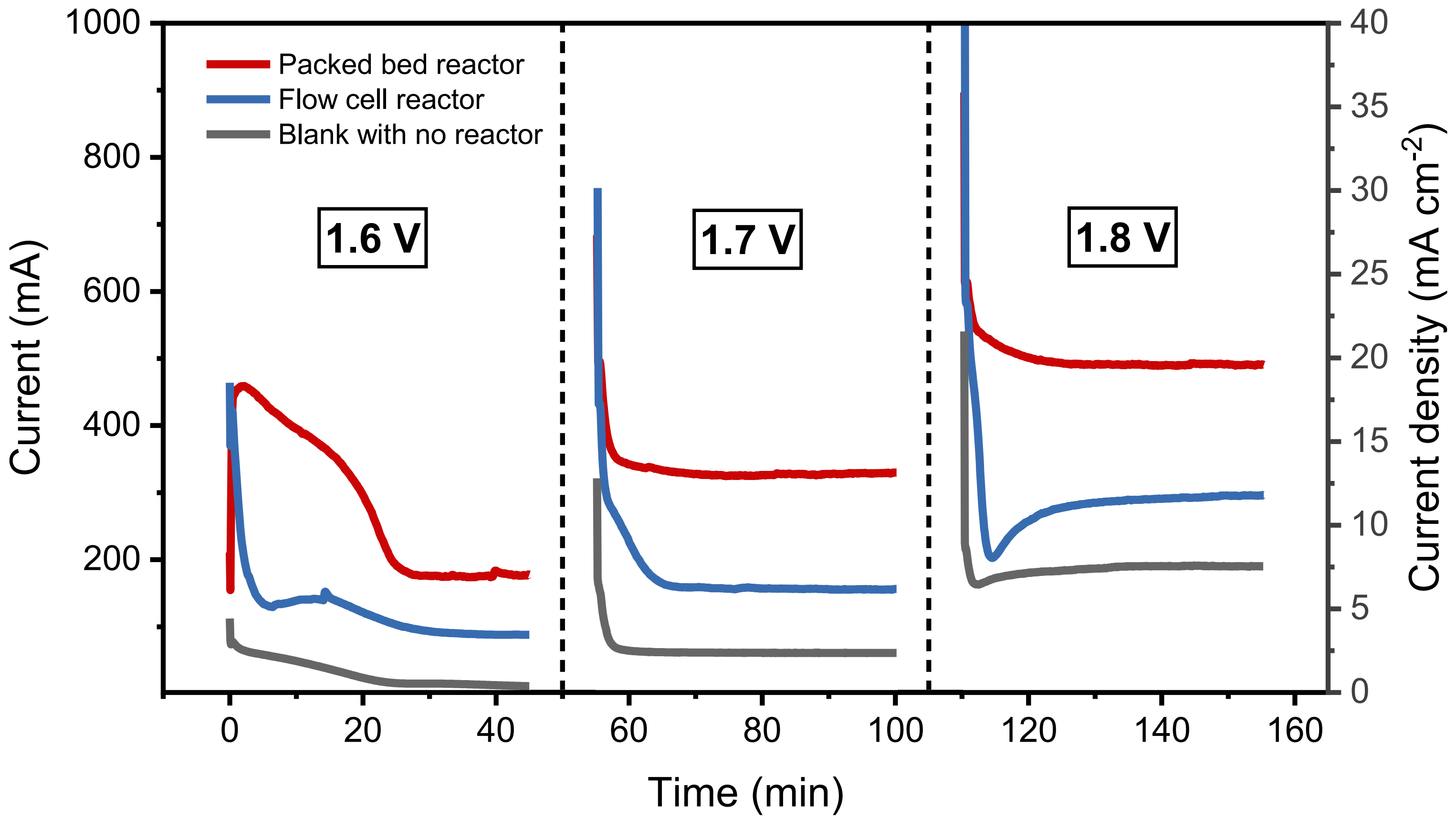
Reactors are part of the same circulation loop along with electrochemical cell and tanks

50 mL of 0.2 M Fe-DIPSO @ 4M NaOH

50 mL of 0.2 M potassium ferrocyanide @ 4M NaOH

Anion exchange membrane

DUAL FLOW ELECTROLYSIS



All stages begin at SoC100 and **reach a quasi-steady state** — a constant current at a constant voltage.

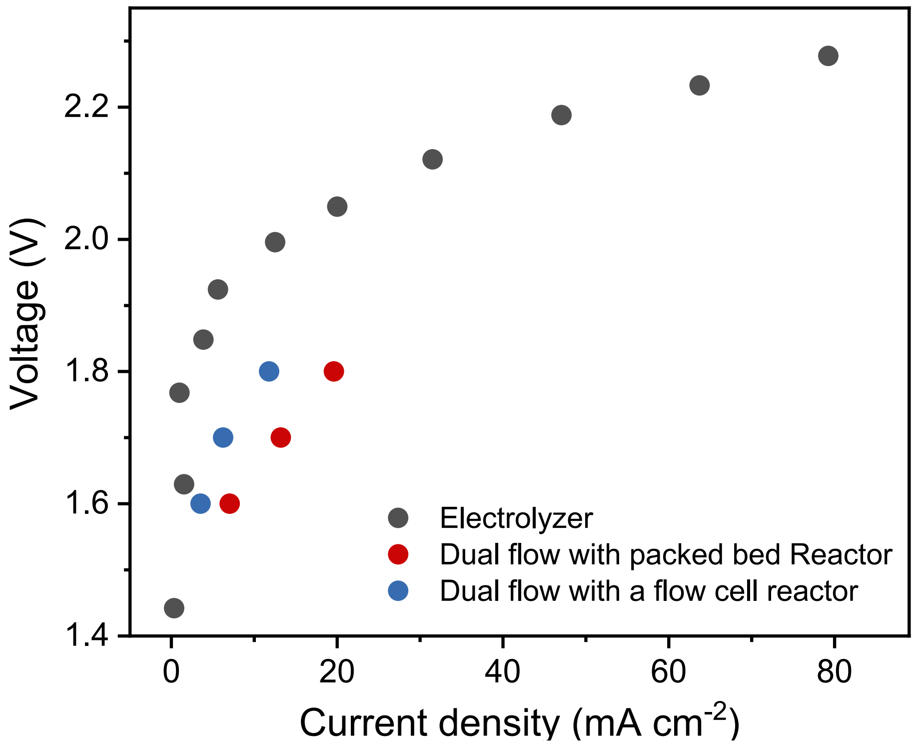
This shows that the **discharge of redox mediators in the reactor is balanced by their charge** in the electrochemical cell.

Quasi-steady SoC of the redox mediators at each stage may differ from 100

The **flow cell reactor outperforms** the others and shows up to 20 mA cm^{-2} and 500 mA at 1.8 V.

Remember that **apparent currents in batch measurements** were up to 1A

HOW GOOD IS THIS GOOD?



Zero-gap electrolysis cell: 6.25 cm^2, 6 M KOH,
Nickel foam electrodes, ZIRFON Separator

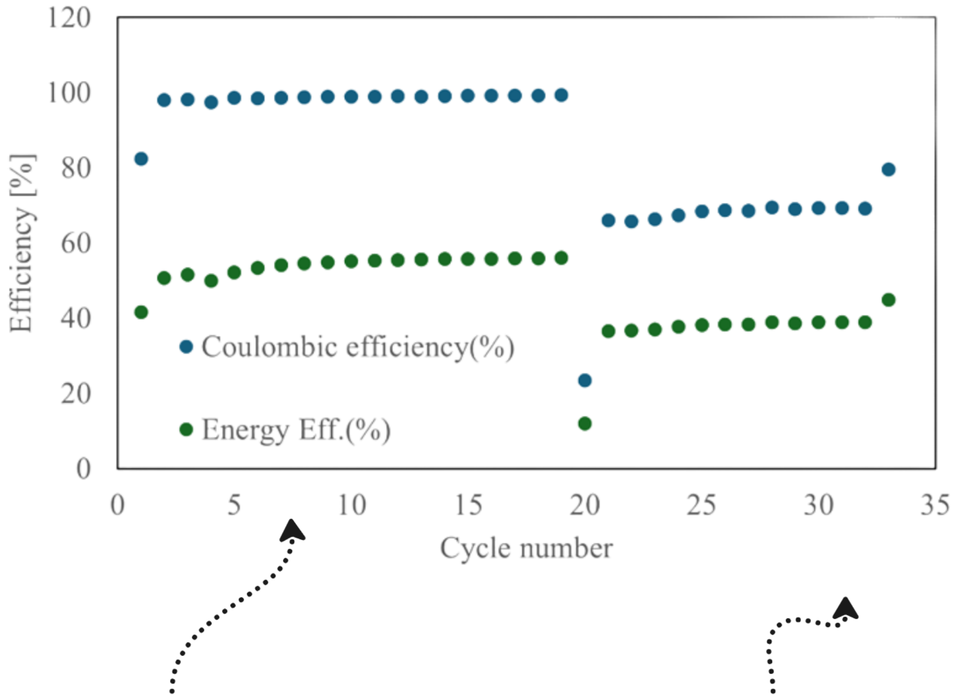
Both **dual-flow setups significantly outperformed** a classic zero-electrolysis cell when tested in our lab.

For a voltage of 1.8 V, the current densities were approximately 2 mA/cm², 12 mA/cm² and 20 mA/cm² for the electrolysis cell, the dual-flow setup with a zero-gap cell reactor and the dual-flow setup with a packed-bed reactor, respectively.

Performance can be increased further by (slightly) increasing temperature, creating more alkaline conditions or switching to a smaller electrochemical cell

CAN WE CYCLE RFB AGAIN?

Packed bed reactor



**Before electrolysis.
Reactors off**

**After electrolysis.
Reactors off**

Not really ☹ At least not in the case of a packed-bed reactor, because the **Raney nickel leaked** from the reactor into the tank and started catalysing HER/OER there -> Reactors need some tweaks and optimizatoin

However, **in the case of the flow electrochemical cell as a reactor**, everything was fine. EE and FE remain roughly the same after the electrolysis;

CONCLUSIONS

- Even though **Fe-DIPSO and Ferricyanide potentials are at the very edge of the thermodynamic zone** required to mediate HER and OER, they can carry out these reactions with Raney nickel as a catalyst
- These **dual-flow batteries**, which utilise a mediator, are **capable of spatially decoupled electrolysis at room temperature in continuous mode** for at least 1.5 hours.
- When equipped with a fixed-bed reactor, the **dual-flow system significantly outperforms the regular alkaline electrolysis cell**, sustaining a current density of around 20 mA/cm^2 at an applied voltage of 1.8 V.
- Notably, the **dual flow system can switch from electrolysis mode to energy storage mode**, albeit accompanied by some EE/FE losses.

DUAL FLOW PROJECT

UNIVERSITY OF TURKU

AARHUS UNIVERSITY

UNIVERSITY OF LIMERICK
OLLSCOIL LUIMNIGH

A!
Aalto University

NORDIC BIOPRODUCTS GROUP

UNIVERSITY OF GREENWICH

Lancaster University

DualFlow (Dual circuit flow battery for hydrogen and value-added chemical production) has received funding from the European Union's Horizon Europe research and innovation programme through the European Innovation Council

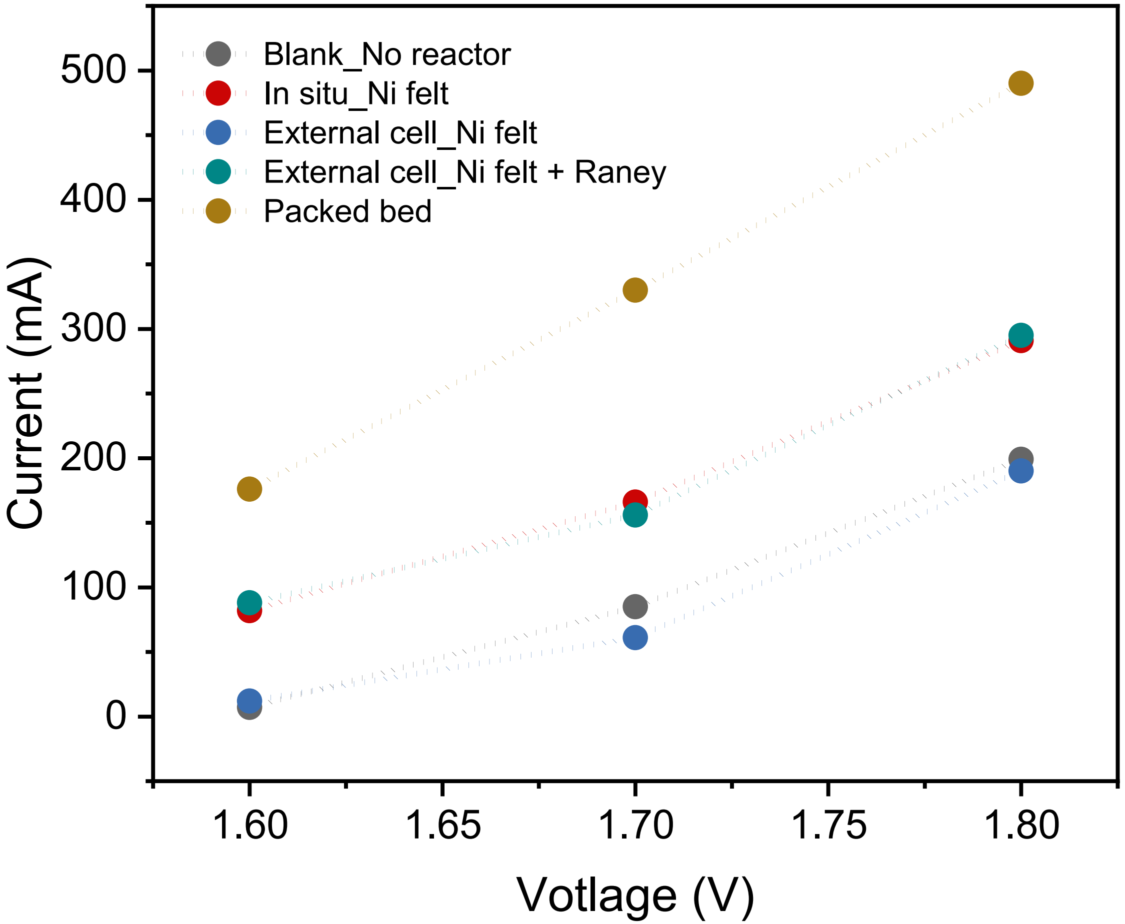
DualFlow

European Innovation Council

AARHUS
UNIVERSITY

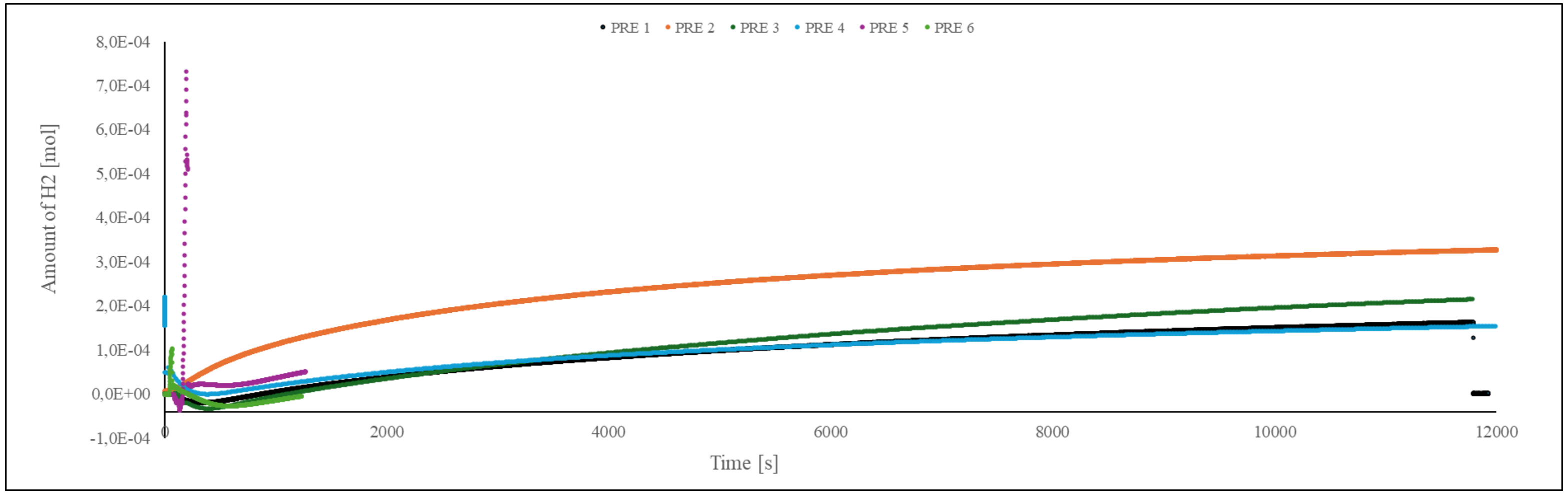
DUAL FLOW. OTHER REACTORS

Reactor	Current@ 1.6 V (mA)	Current @ 1. 7 V (mA)	Current @1.8 V (mA)
Blank	7	85	199
In situ (Ni felt)	82	166	291
In situ (Ni felt + raney)	82	145	282
Extern cell (Ni felt)	12	61	190
Extern cell (Ni felt Raney)	88	156	295
Packed bed	176	330	490



BATCH HER

Experiment number	Catalyst	Amount of catalyst [g]	Total H_2 produced [mol]	Total H_2 expected [mol]	k [s^{-1}]	FE [%]
PRE 1	Nickel <150μm	1.0	$1.63*10^{-4}$	$2.5*10^{-3}$	$1.46*10^{-5}$	6.53
PRE 2	Nickel <150μm	1.0	$3.76*10^{-4}$	$2.46*10^{-3}$	$5.69*10^{-5}$	15.27
PRE 3	Nickel <150μm	2.0	$3.73*10^{-6}$	$2.6*10^{-3}$	$7.03*10^{-7}$	0.14
PRE 4	Nickel <150μm	1.0	$2.2*10^{-4}$	$2.0*10^{-3}$	$1.2*10^{-5}$	10.82
PRE 5	Raney nickel	0.37	$7.3*10^{-4}$	$2.6*10^{-3}$	$1.16*10^{-2}$	27.97
PRE 6	Raney nickel	0.076	$1.03*10^{-4}$	$6.5*10^{-3}$	$1.99*10^{-3}$	3.96



BATCH OER

OER screening	KOH [M]	NaOH [M]	Ferri [M]	Temp [degC]	Catalyst	Catalyst [g]	ORP start [V]	ORP end [V]	ORP change	Oxidation start [%]	Oxidation end [%]	Oxidation change
EXP 1	-	-	0,25	Room temp	Nikkel <150µm	4	1,93	1,93	0,01	-	-	
EXP 2	-	4	0,25	Room temp	Pt/C	0,05	1,89	1,85	0,04	99,8	99,0	0,8
EXP 3	-	4	0,25	Room temp	Nikkel <150µm	4	1,90	1,85	0,05	99,9	99,4	0,5
EXP 4	-	4	1	Room temp	Nikkel <150µm	4	1,90	1,85	0,05	99,8	98,6	1,2
EXP 5 (7)	-	4	0,5	Room temp	Rayney nikkel	2	1,91	1,86	0,04	99,9	99,5	0,4
EXP 6 (8)	-	4	0,5	Room temp	Rayney nikkel	2	1,91	1,85	0,06	100,0	99,4	0,5
EXP 7	-	4	0,5	Room temp	Rayney nikkel	1	1,90	1,86	0,04	99,9	99,6	0,3
EXP 8	-	4	0,5	Room temp	Nikkel felt 0,25mm	9,7	1,89	1,86	0,03	99,8	99,5	0,3
EXP 9	-	4	0,5	35	Rayney nikkel	1	1,89	1,85	0,04	99,9	99,5	0,4
EXP 10	-	4	0,5	50	Rayney nikkel	1	1,87	1,83	0,04	99,8	98,5	1,3
EXP 11	4	-	0,25	Room temp	Rayney nikkel	1	1,88	1,83	0,05	99,8	98,3	1,5
EXP 12	6	-	0,25	Room temp	Rayney nikkel	1	1,87	1,86	0,01	99,5	-	-
EXP13	6	-	0,25	50	Rayney nikkel	1	1,86	1,78	0,08	99,7	91	8,7

CYCLING BEFORE AND AFTER. PACKED BED