Fabrication of formate dehydrogenase biocathodes for bioelectrochemical CO_2 conversion

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Outline

1. Introduction
2. Enzymatic CO_2 Biorefinery
3. Fabrication of enzymatic biocathodes
4. Conclusions

1. Introduction

Pre-industrial level

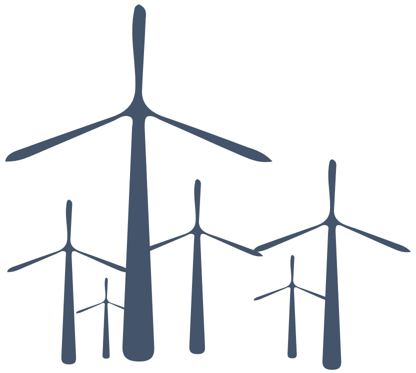
270 ppm

In 2015 exceeded

400 ppm

CO_2 serves as earth thermoregulation

Global warming → climate changes



CO_2 emission reduction strategies:
(Paris Agreement, 2015)

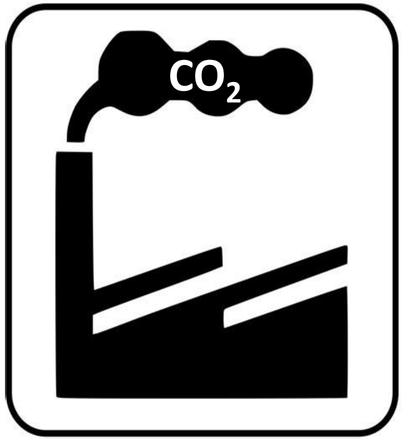
Upstream:

Renewable energies

Downstream:

CCSU (carbon capture, storage and utilization) processes

2. Enzymatic CO_2 Biorefinery



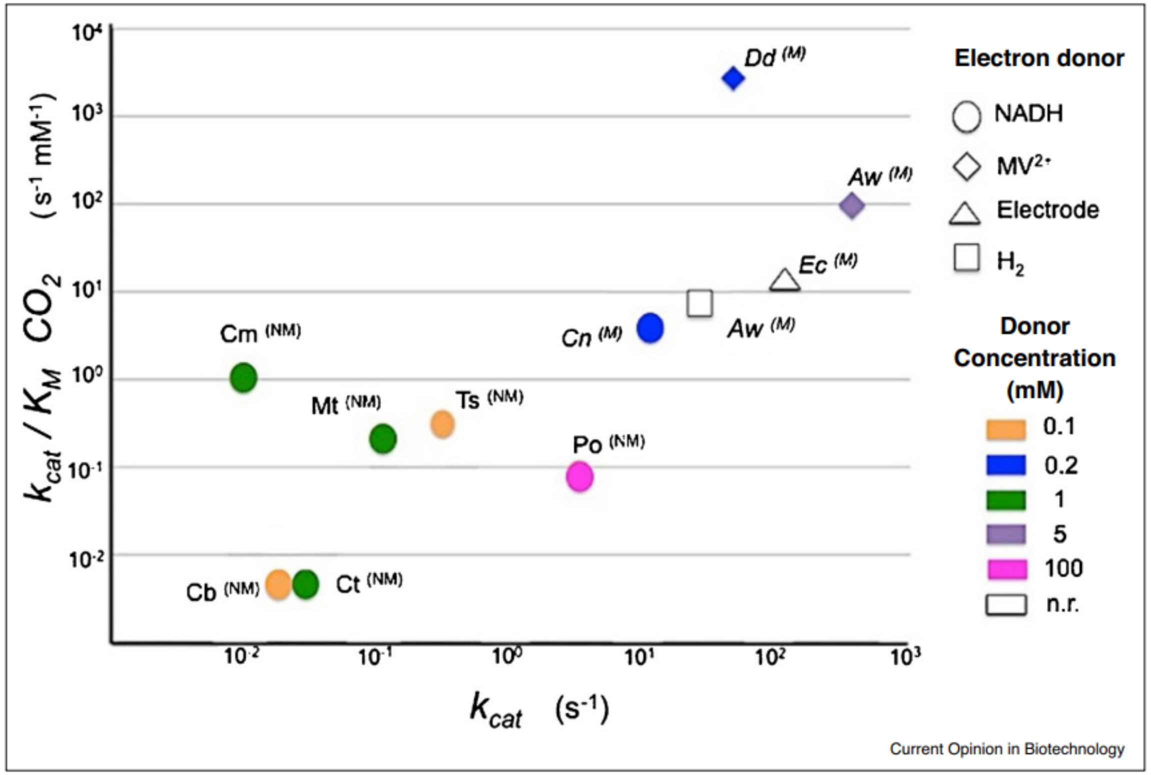
CO_2 capture and conversion → Formate dehydrogenase → Formic acid

CO_2 capture and conversion → Carbon monoxide dehydrogenase → Carbon monoxide

Biogas upgrading → Nitrogenase → Methane

2. Enzymatic CO_2 Biorefinery

Kinetic properties of FDH catalyzed CO_2 reduction



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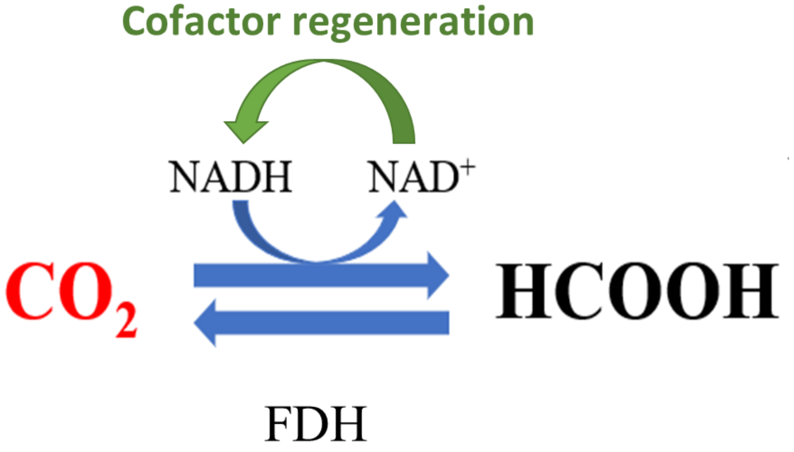
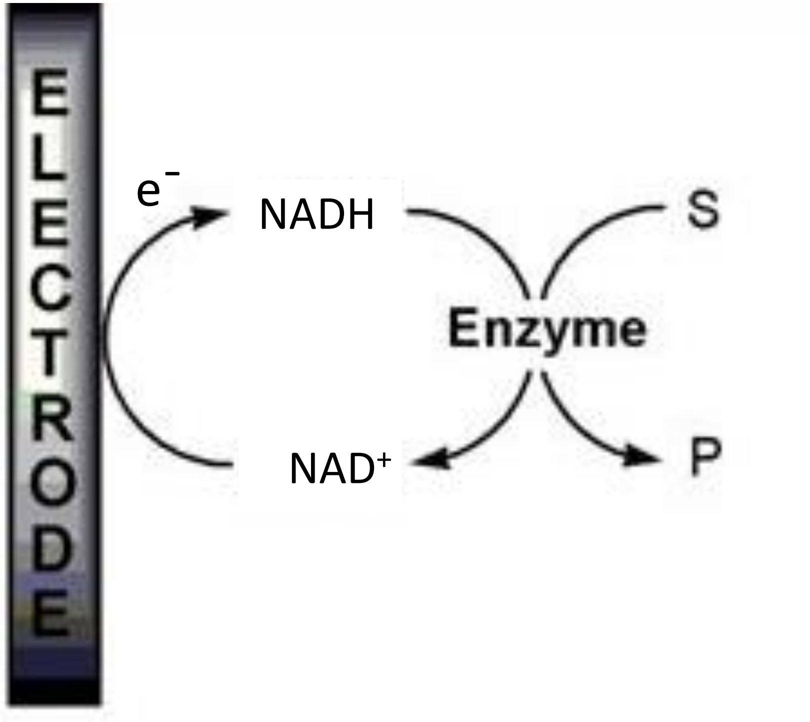
- Most FDH are NADH dependent
- NADH is needed in high concentrations
- NADH has high costs



2. Enzymatic CO_2 Biorefinery

Electrochemical regeneration

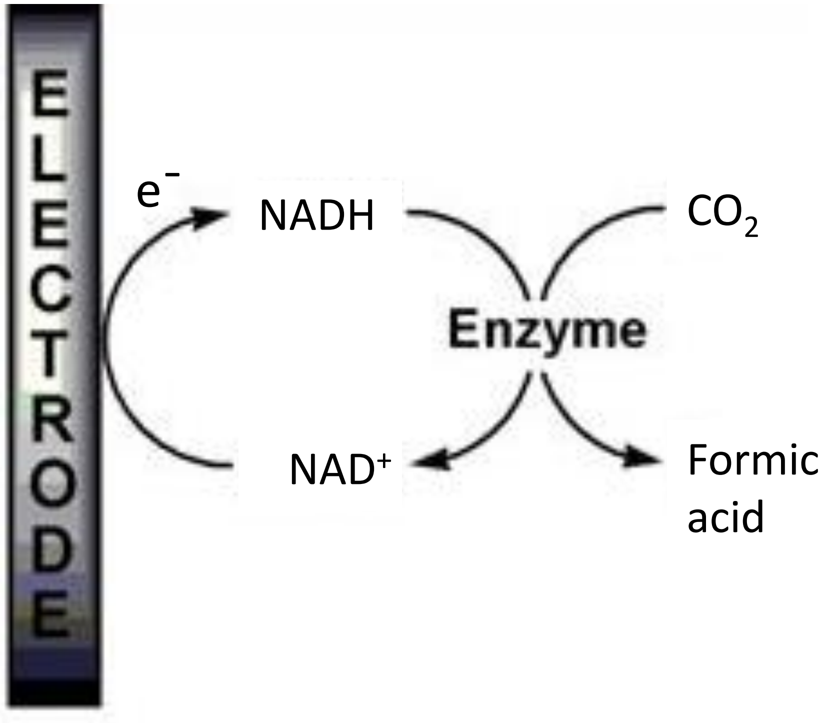


- Use of clean, renewable electrical energy
- Broad applications

- Low TTN,
- low selectivity
- Electrode fouling

2. Enzymatic CO_2 Biorefinery

Electrochemical regeneration



- Use of clean, renewable electrical energy
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- Low TTN
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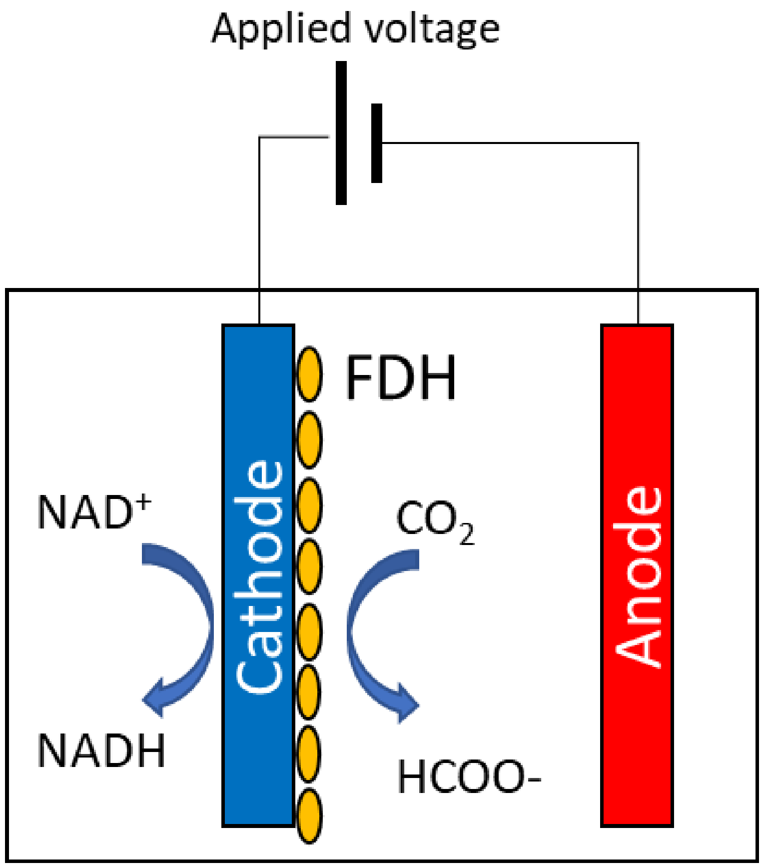
Novel electrode materials are studied

Electrochemical cell configuration



Electrode

Good compromise for both enzymatic support and electrocatalyst

NADH recycling

Chemical catalysts

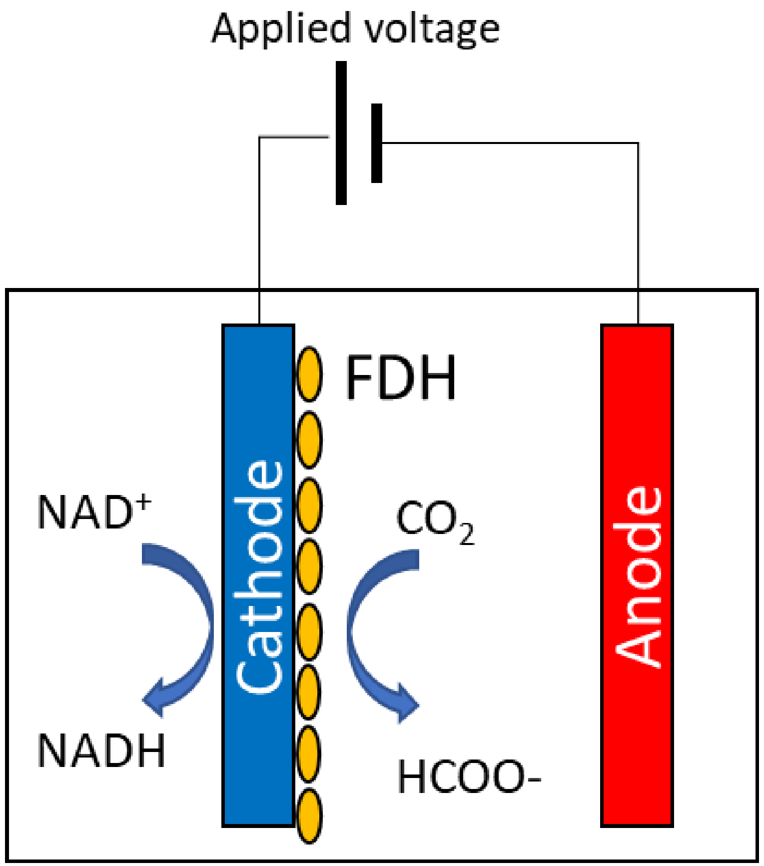
Active NADH

FDH immobilization

Modifications of the electrode surface chemistry

Reusability advantages

Electrochemical cell configuration



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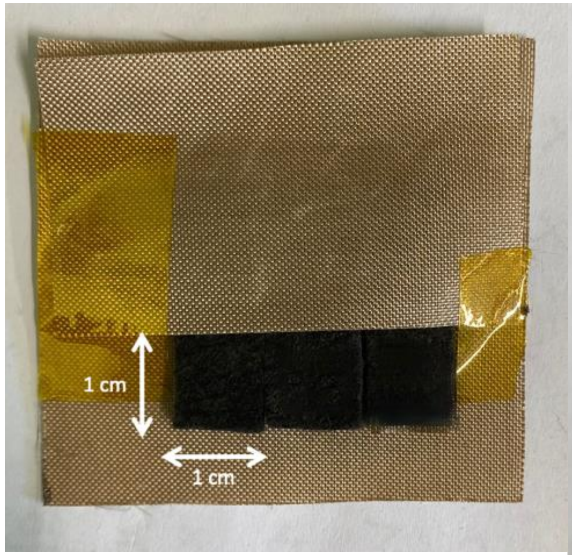
3. Fabrication of enzymatic biocathodes

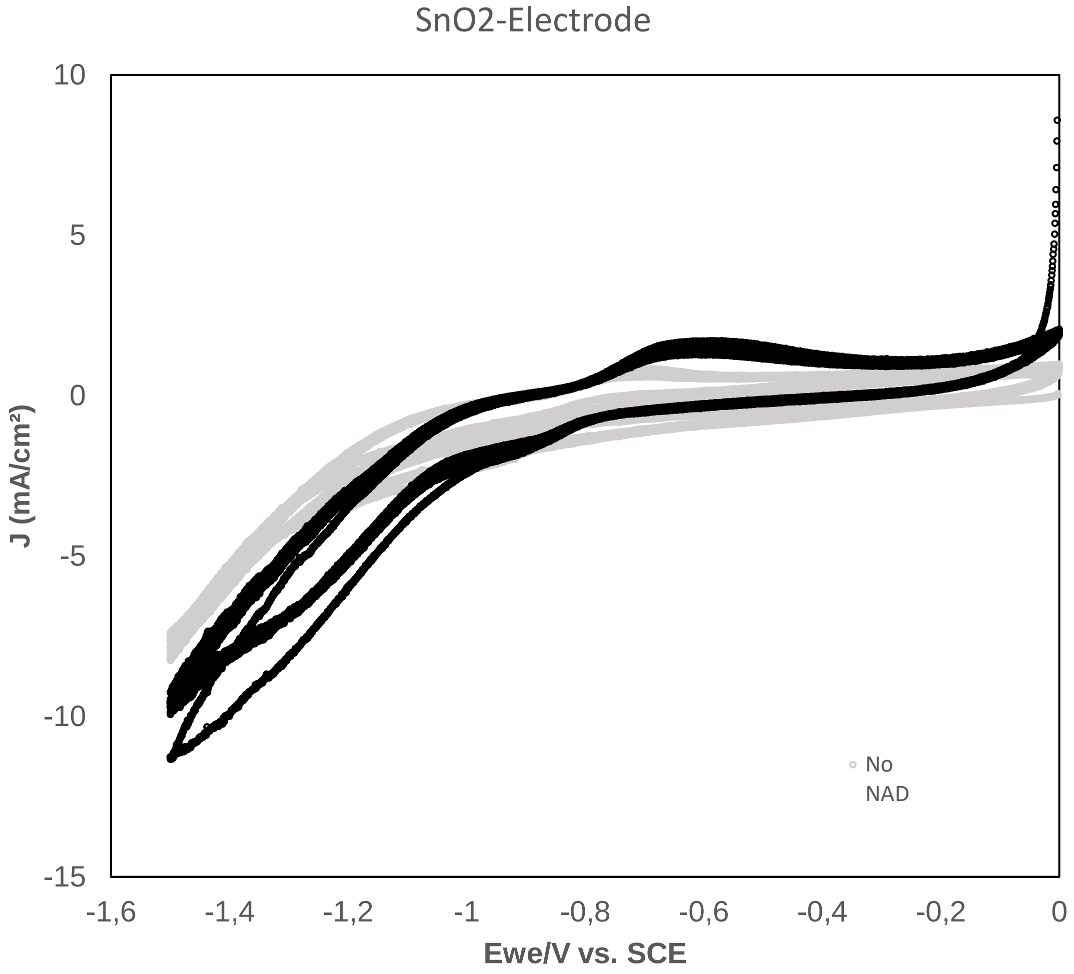
Deposition of nanoparticles on electrode

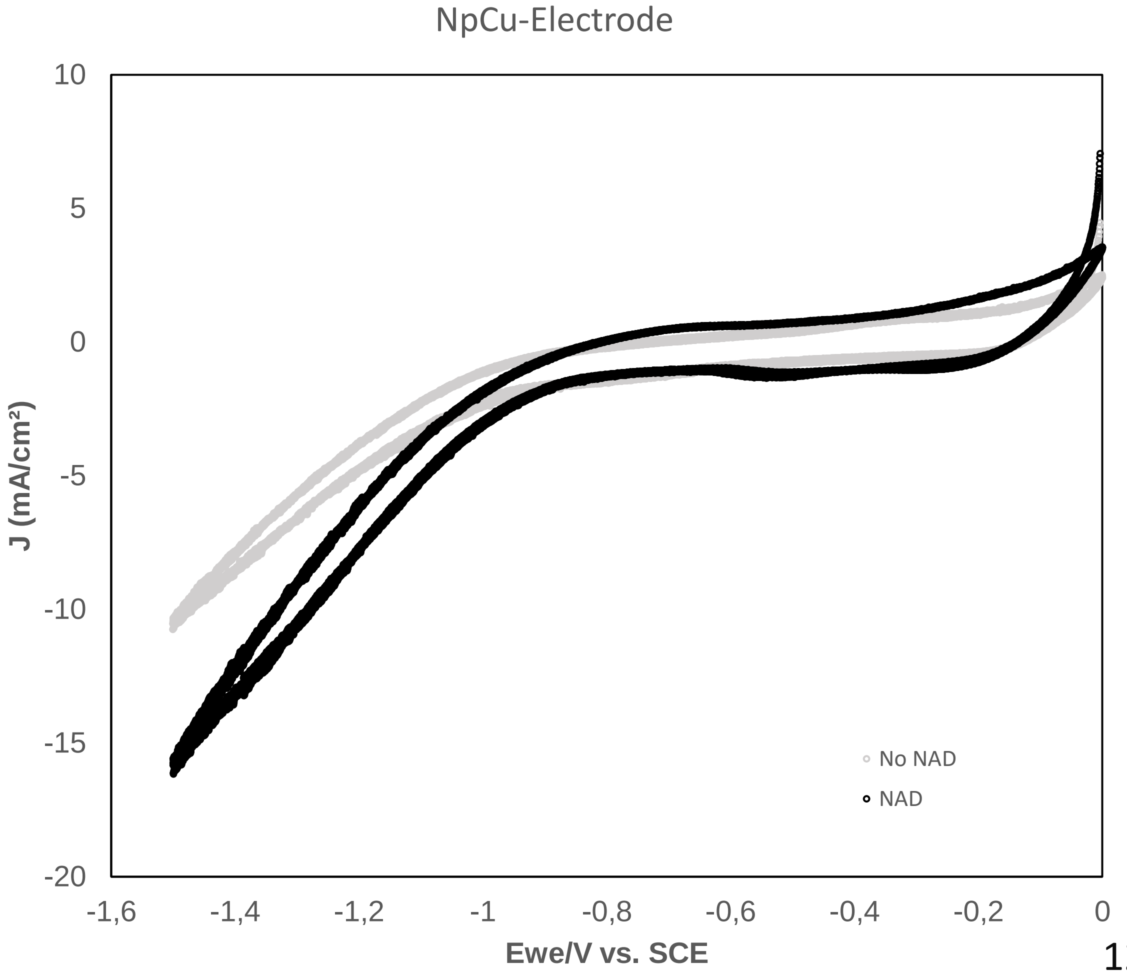
	Catalyst 1		Catalyst 2	
Material	SnO_2	Aldrich, <100 nm	NpCu	Aldrich, 40-60 nm
Catalyst loading (mg/cm^2)	3.5	-	3.5	-
Ligand	Nafion	Aldrich, 5%	Nafion	Aldrich, 5%
Catalyst/Ligand ratio	12	%	12	%
Solvent	Isopropanol	Aldrich, 99.8%	Isopropanol	Aldrich, 99.8%
Solvent/Nafion+Catalyst ratio	2.2:1	-	2.2:1	-



3. Fabrication of enzymatic biocathodes

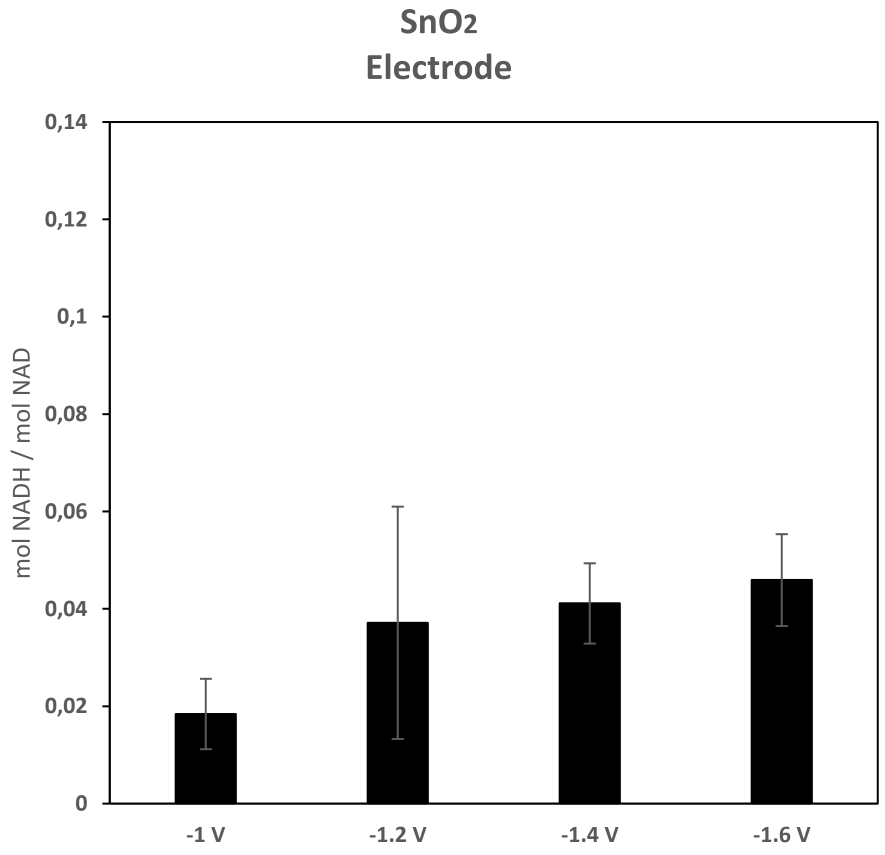
Cyclic voltammetry of NP-modified electrodes in presence and absence of NAD$^+$

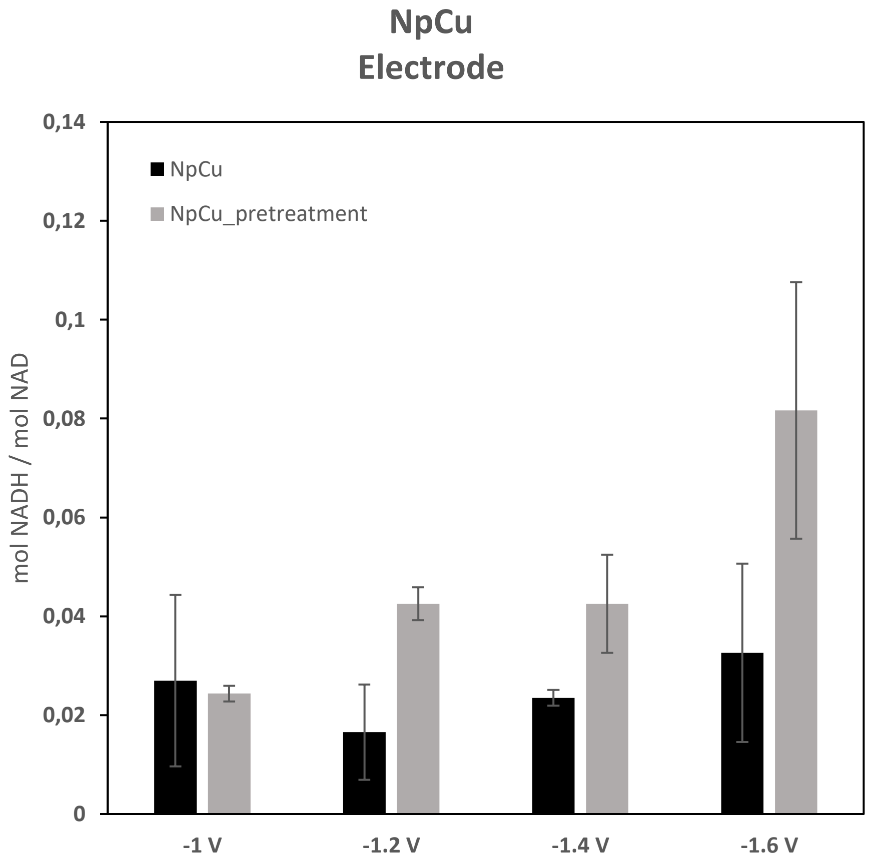




3. Fabrication of enzymatic biocathodes

Effect of catalyst material on NADH regeneration



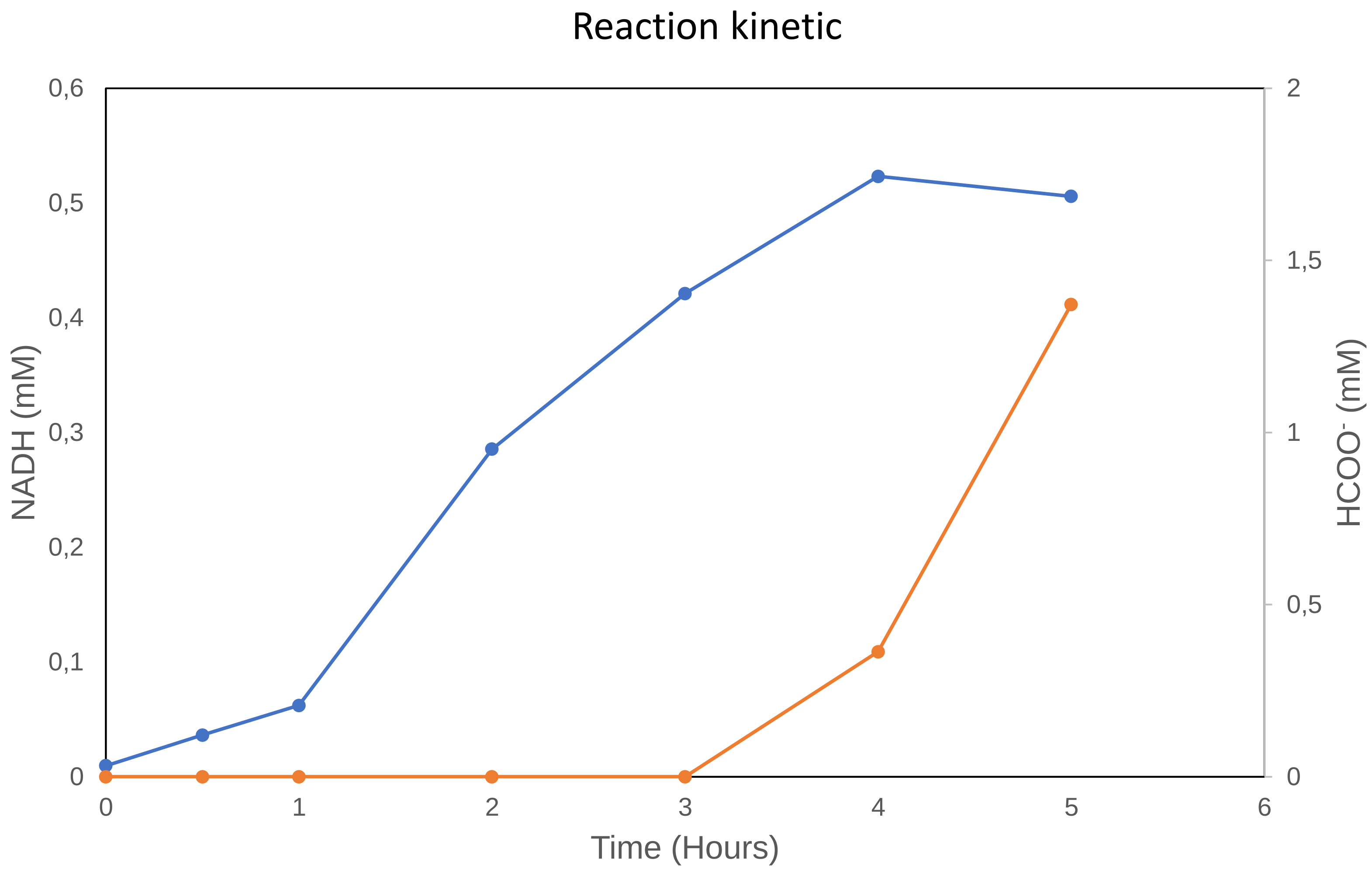


3. Fabrication of enzymatic biocathodes

Reaction conditions

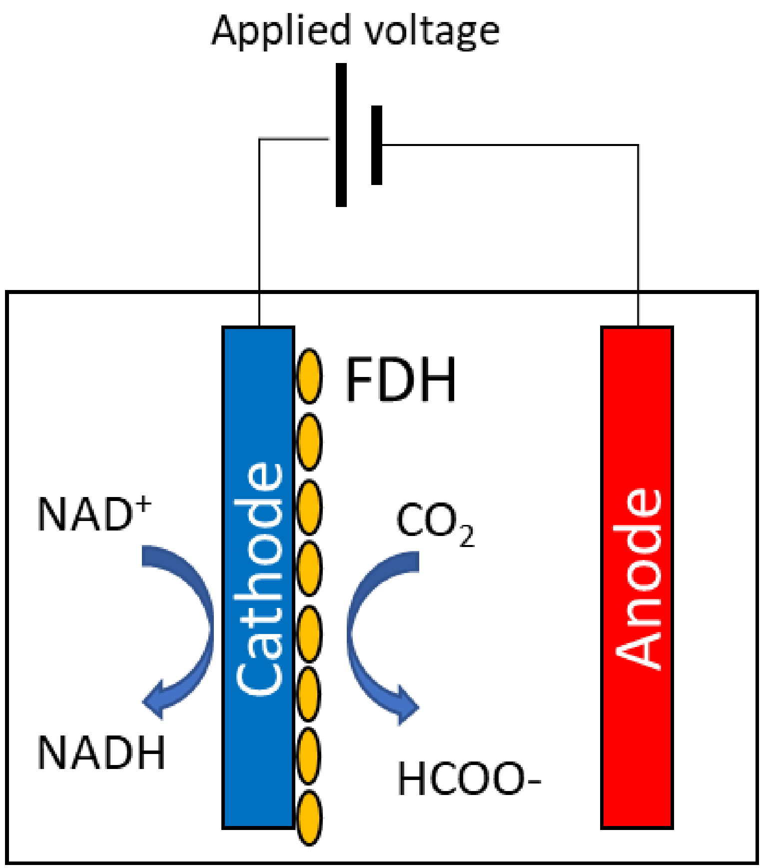
CO_2 flow: 38 Nml/min
Phosphate Buffer 250 mM (pH 8.5)
NAD^+ 1 mM

Total enzymatic units: 0.69 U
pH final: 7.6



2. Enzymatic CO_2 Biorefinery

Electrochemical cell configuration



Electrode

Good compromise for both enzymatic support and electrocatalyst

NADH recycling

Chemical catalysts

Active NADH

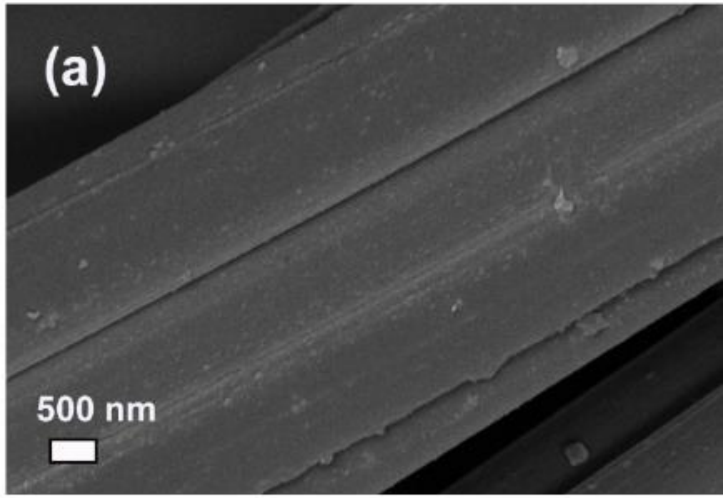
FDH immobilization

Modifications of the electrode surface chemistry

Reusability advantages

3. Fabrication of enzymatic biocathodes

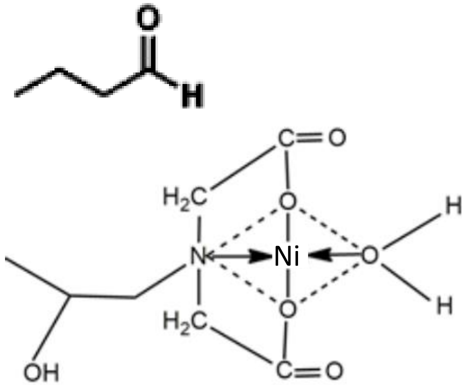
Activation of the electrode



1. GPTMS
5% vol.
105 °C, 5h

2. Iminodiacetic acid
2 M
pH 11, 4 h, r.t.

3. $NiSO_4$
200 mM
2h, r.t.

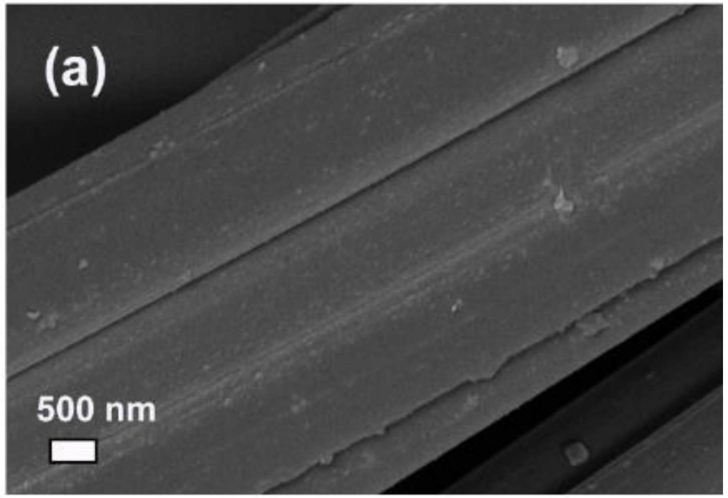


CF IDA – Ni^{2+}

Electrode	Carbon felt (CF)	Base treatment KOH 1 M, 100 °C	Acid treatment HNO_3 1 M, 100 °C
Specific surface area ($m^2 \cdot g^{-1}$)	0.23	0.41	161.53
IDA-Ni^{2+} groups ($\mu mol \cdot g^{-1}$)	1.38	5.36	5.02

3. Fabrication of enzymatic biocathodes

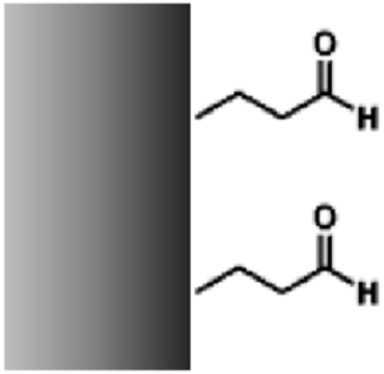
Activation of the electrode



1. GPTMS 5% vol. 105 °C, 5h

2. H_2SO_4 0.1 M 85 °C, 5h

3. $NaIO_4$ 0.1 mM 2h, r.t.

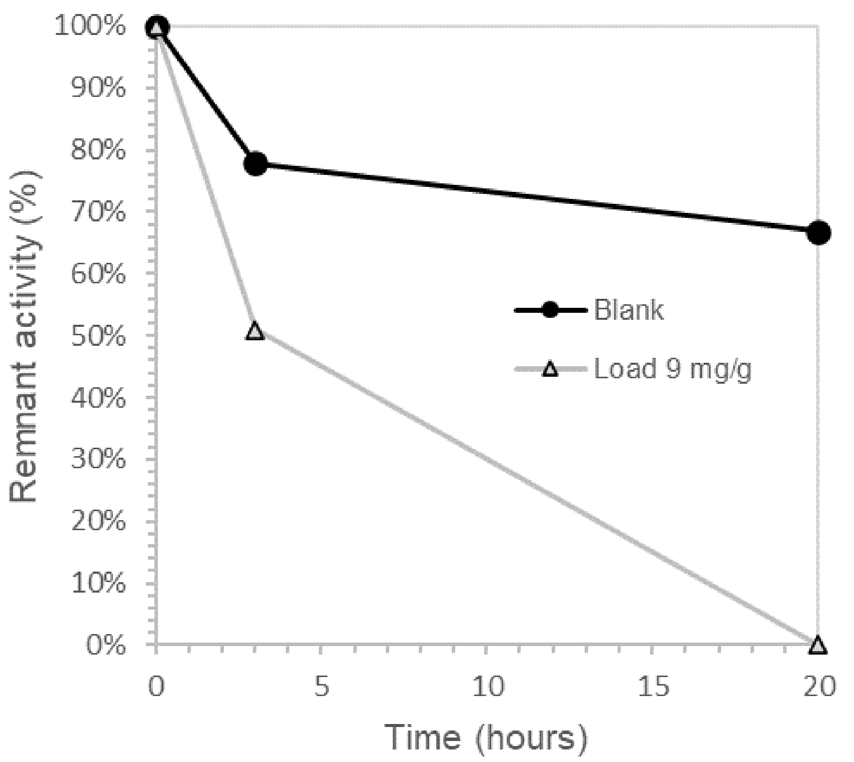


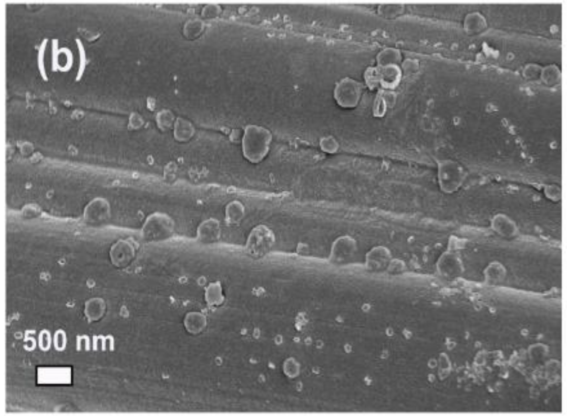
CF Glyoxyl

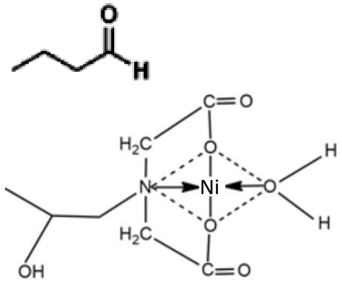
Electrode	Carbon felt (CF)	Base treatment KOH 1 M, 100 °C	Acid treatment HNO_3 1 M, 100 °C
Specific surface area ($m^2 \cdot g^{-1}$)	0.23	0.41	161.53
Aldehyde groups ($\mu mol \cdot g^{-1}$)	800	Not measured	1500

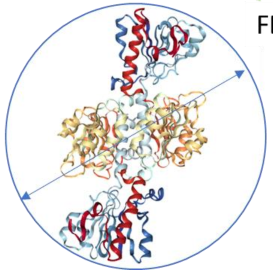
3. Fabrication of enzymatic biocathodes

Immobilization kinetic









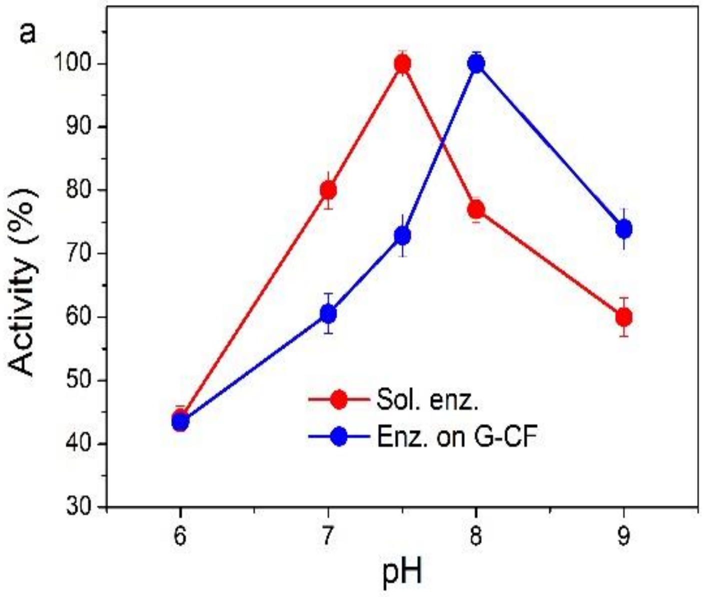
FDH from *C.boidinii*

$\emptyset = 5.5\ nm$

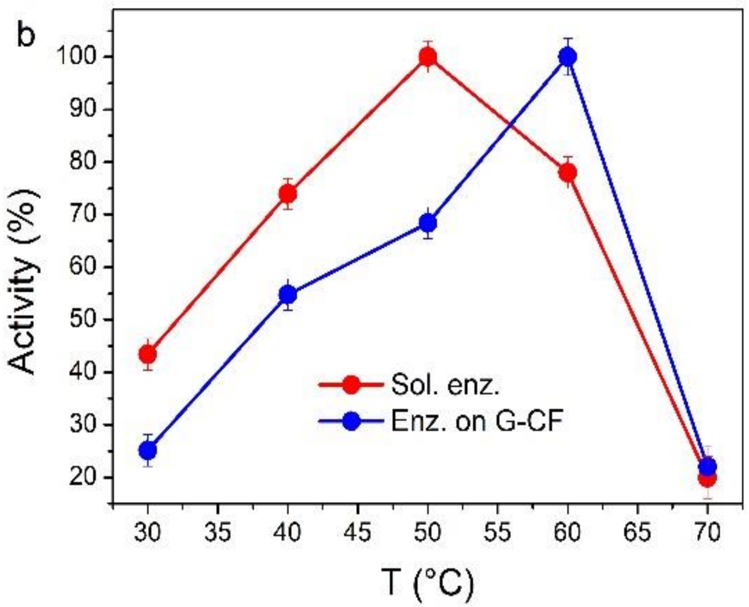
3. Fabrication of enzymatic biocathodes

Characterization of the immobilized FDH

Effect of pH



Effect of temperature



Shift of highest activity conditions to higher temperatures and pHs

Ottone *et al. Chemistry Open (accepted)*

3. Fabrication of enzymatic biocathodes

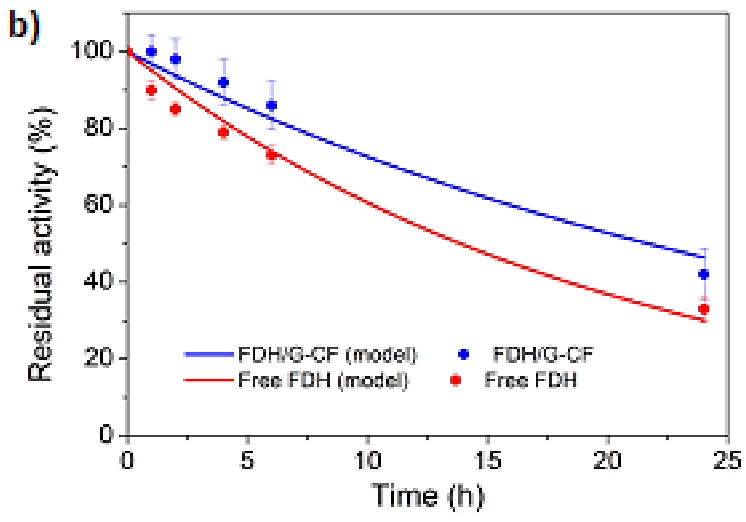
Characterization of the immobilized FDH

	SA (U/g)	RA (%)	Y_{PI} (%)	L_P (mg FDH/gCF)
CF-IDA Ni^{2+}	0.51 ± 0.07	4 ± 1	45	1.3
CF-KOH IDA Ni^{2+}	0.89 ± 0.8	7 ± 1	75 ± 12	2.2 ± 0.4
CF-HNO_3 IDA Ni^{2+}	1.26 ± 0.13	10 ± 1	79 ± 5	2.4 ± 0.25
CF-Glyoxil	0.265 ± 0.09	2.1 ± 0.75	21.2 ± 1	0.85 ± 0.04

$$SA\ (U \cdot g^{-1}) = \frac{A\ (U)}{m_{CF}(g)}$$

$$RA(\%) = \frac{SA_{measured}}{SA_{teoretical}} \cdot 100$$

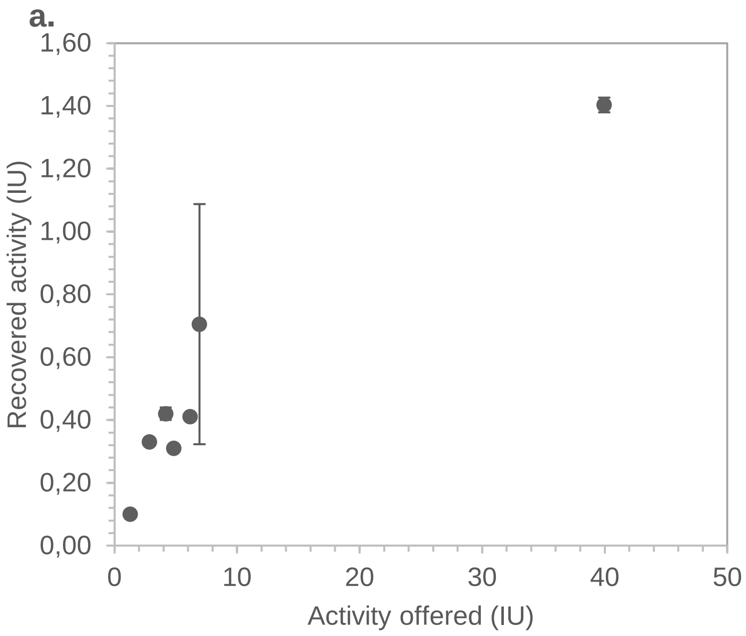
$$Y_{PI}(\%) = \frac{C_{P\_0} - C_{P\_end}}{C_{P\_0}} \cdot 100$$

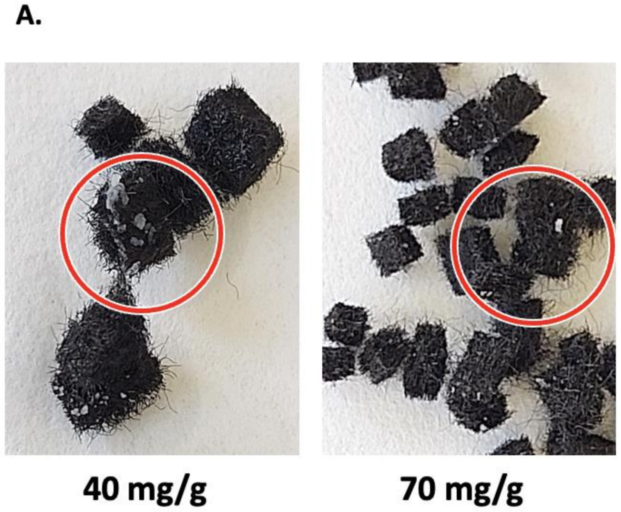


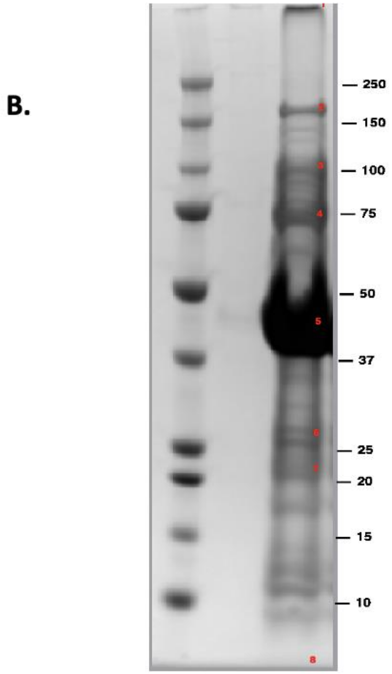
Similar stability with respect to free enzyme

3. Immobilization of FDH on modified electrodes

Effect of enzyme loading



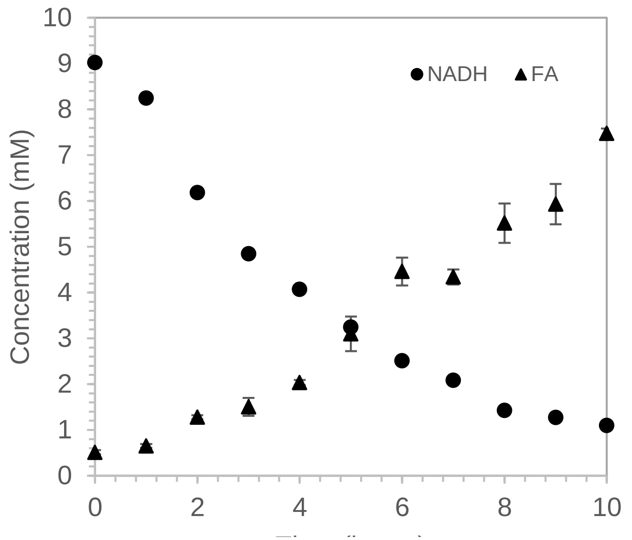


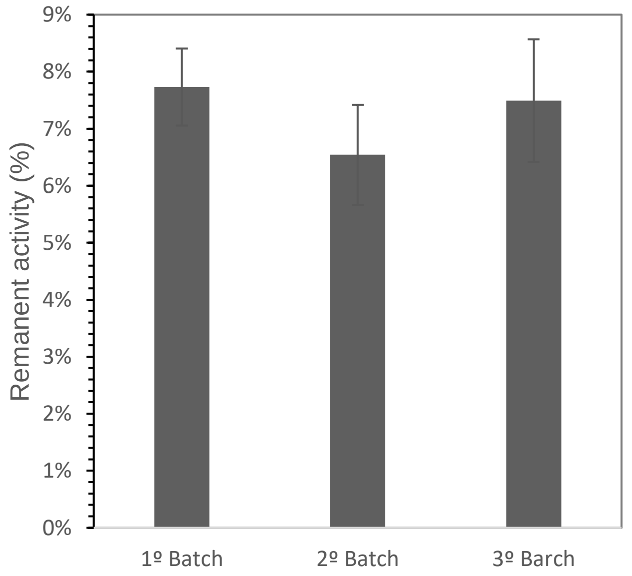


Enzyme Loading (mg/gCF)	3	6	9	12	15	40	70
Specific recovered activity (IU/g)	0.98±0.14	3.13±1.18	4.18±1.37	3.01±0.46	3.88±1.34	8.99±7.8	13.48±0.46
Immobilization activity yield (%)	8	11.7±0.3	8.3±0.2	6.5	6.6	13	3.5
Protein immobilization yield (%)	84±2	91	94	92	91	83±18	77±5
Loaded protein (mg/gCF)	2.8±0.07	5.1	7.9±0.32	11±0.13	13.1±0.21	31.5±6.8	49±2.69

3. Fabrication of enzymatic biocathodes

Production of formic acid by reducing CO_2 as a substrate in a 8 bar reactor





Maureira *et al. (manuscript)*

3. Conclusions

- ✓ Efficient NADH regeneration is necessary for enzymatic CO_2 biorefinery.
- ✓ The deposition of nanoparticles on the electrode surface is a promising strategy for NADH regeneration
- ✓ Acid treatment increases the CF surface area
- ✓ IDA- Ni^{2+} treatment yield to biocathodes with higher SA and RA
- ✓ The immobilization of FDH on CF permits the reusability of the electrode

3. Acknowledgements

International collaborations

- FONDECYT 11180967. Electrochemical hydrogenation of CO_2 with CuO-ZnO based electrode and formate dehydrogenase as co-catalyst .
- RECYCLES EU project Nº 872053.

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