Integrating biomass valorization with electrolytic hydrogen production:

challenges and opportunities

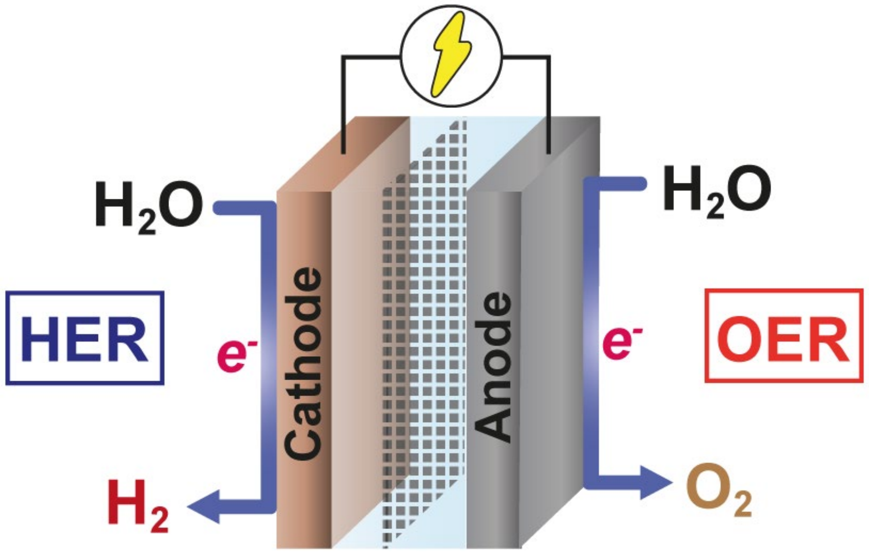
Daniel Martín-Yerga

Department of Chemistry / Nanoscience Center
University of Jyväskylä (Finland)

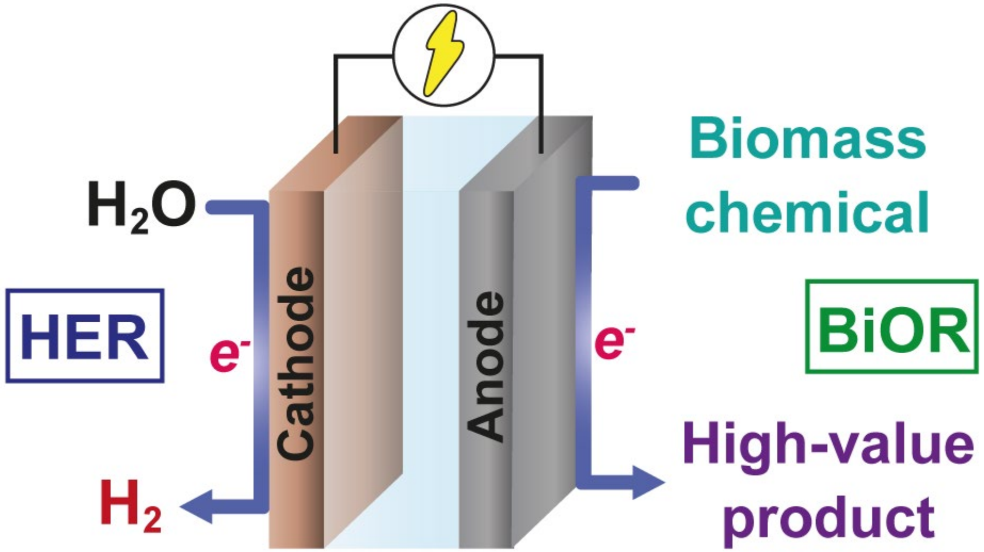
Email: dmartiny@jyu.fi

Integrating biomass in water electrolysis

WATER ELECTROLYSIS



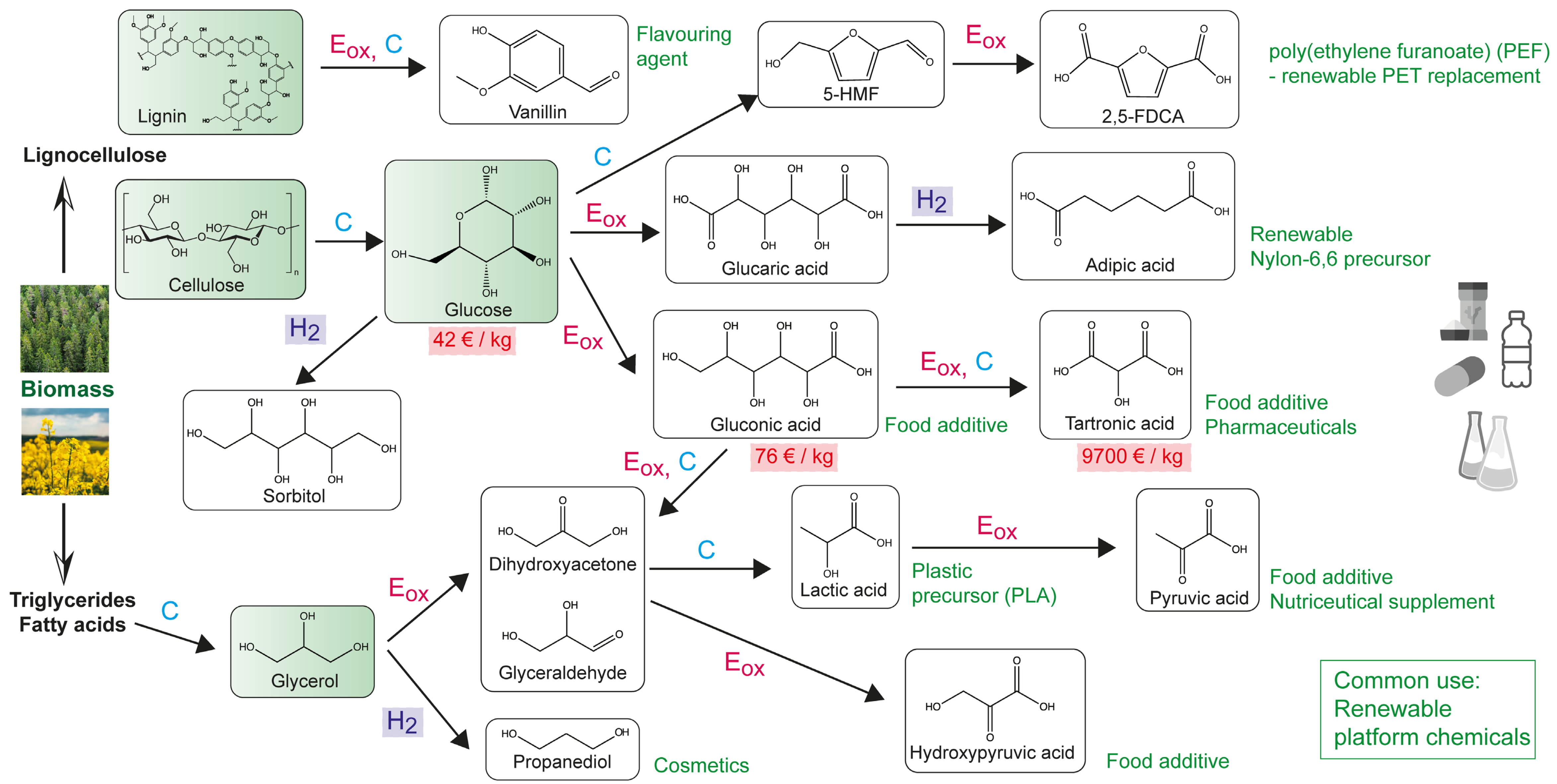
BIOMASS CO-ELECTROLYSIS



Three key advantages for biomass co-electrolysis vs water electrolysis

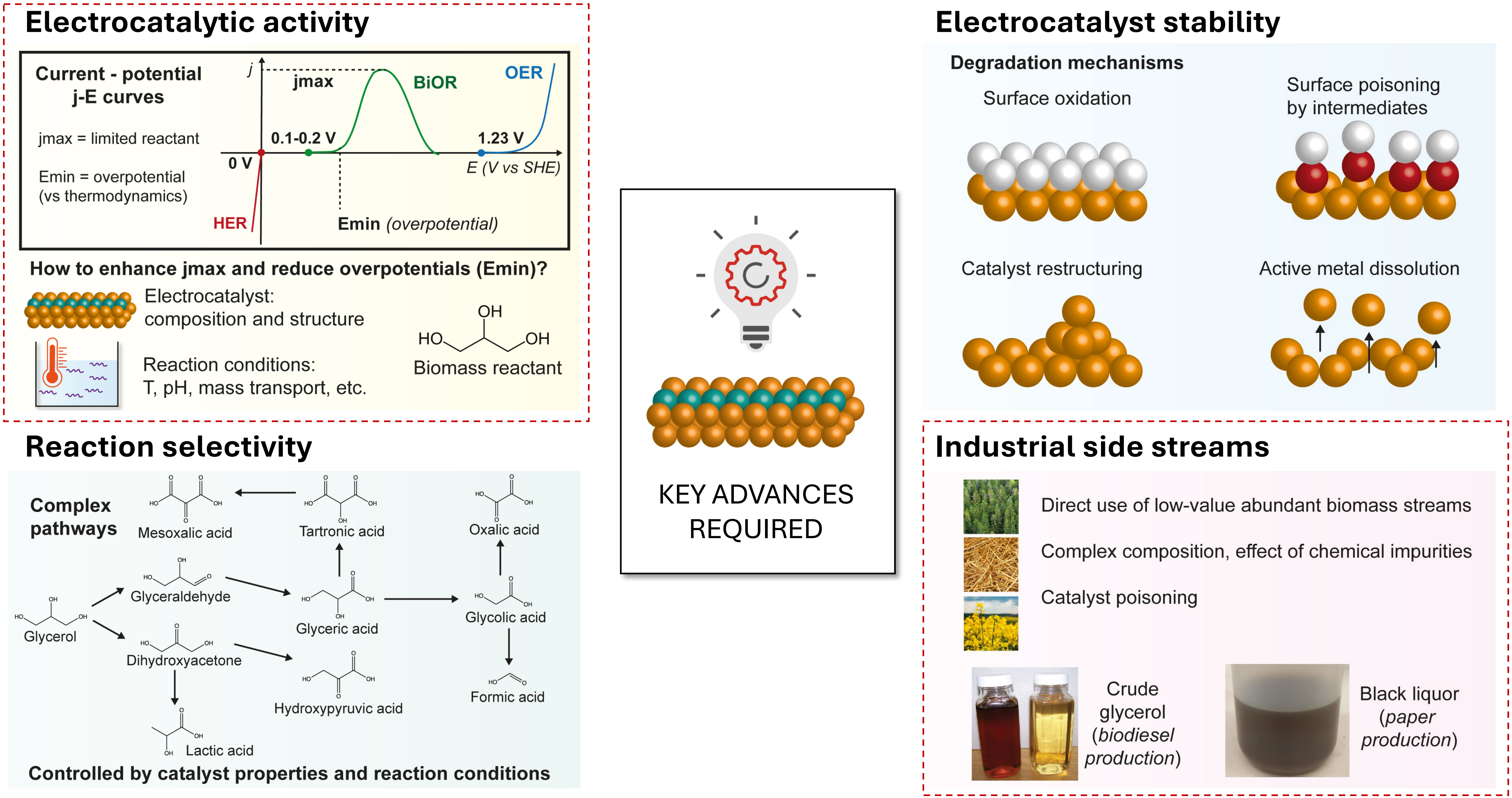
- BiOR thermodynamics (typically E_{BiOR} = 0.1-0.2 V) vs energy-intensive OER thermodynamics (E_{OER} = 1.23 V)
- Carbon-based platform chemicals vs O_2 as anodic product (less valuable)
- Membrane-free electrolyzer (simpler operation) vs membrane-based electrolyzer (to prevent H_2/O_2)

Opportunities in biomass co-electrolysis



*Prices from Sigma-Aldrich

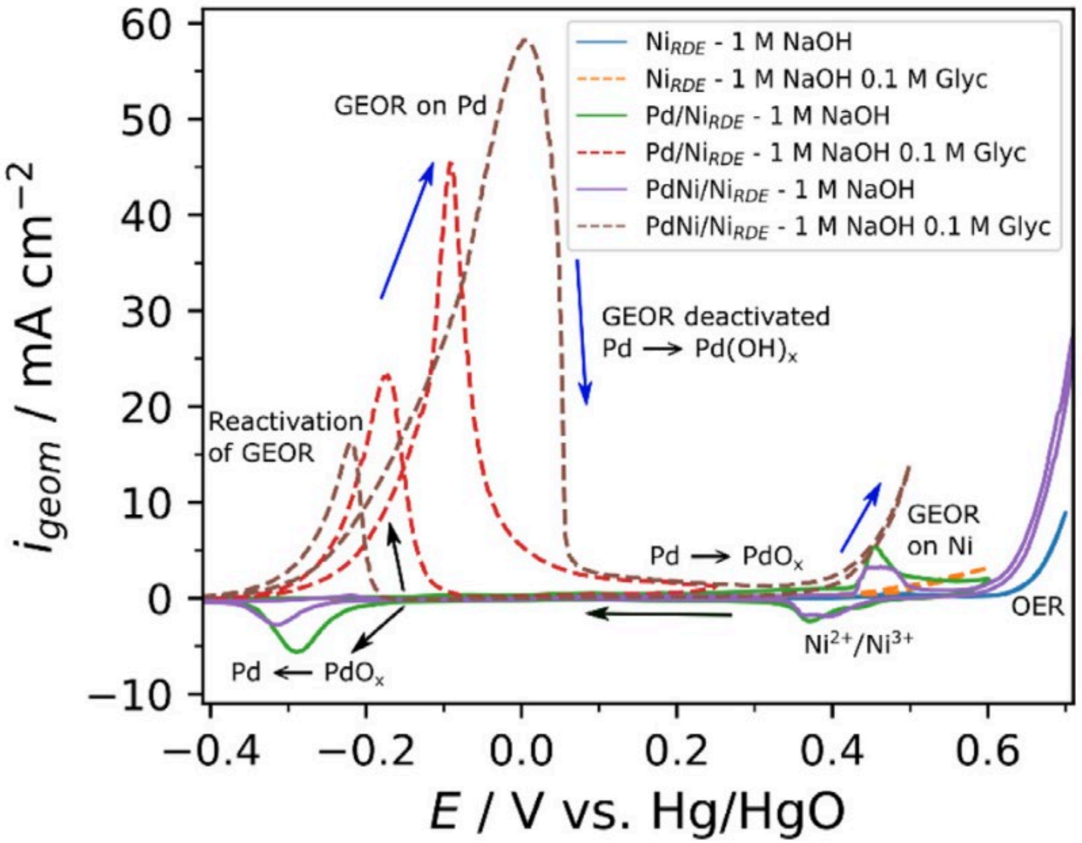
Challenges in biomass co-electrolysis: BiOR electrocatalysis



Factors controlling activity in BiORs

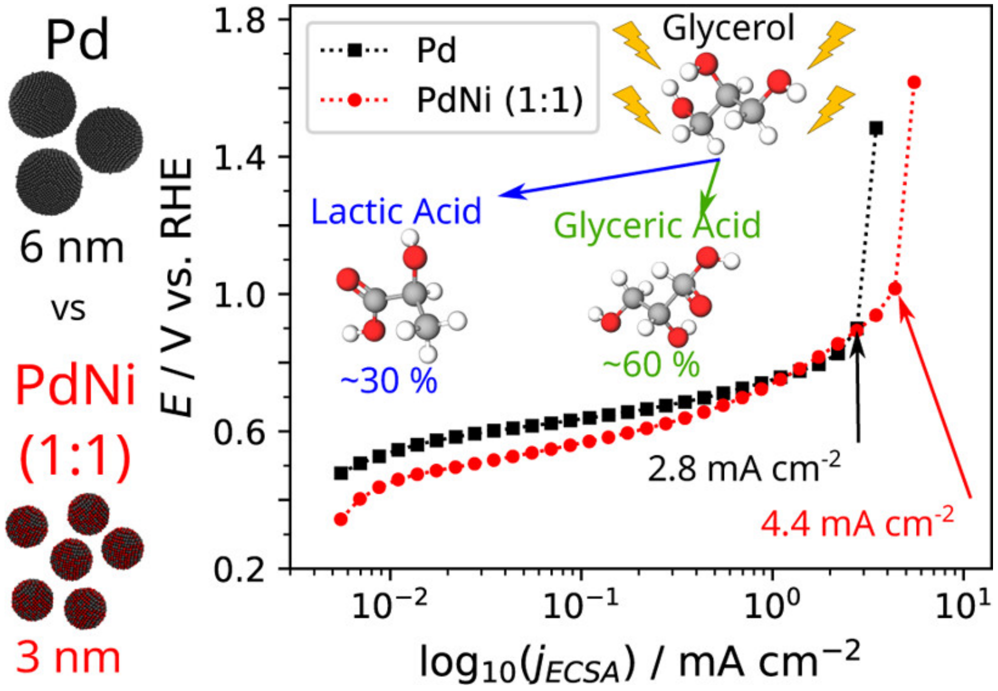
Electrocatalytic material: Ni vs Pd vs PdNi

Glycerol electro-oxidation on Ni, Pd, and PdNi



Significant difference in overpotentials (Pd-based vs Ni)

Decreasing noble metal content: Pd vs PdNi



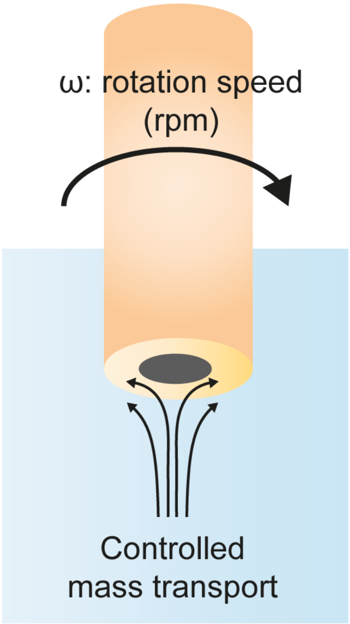
Higher specific and mass activities: PdNi > Pd
Similar C3 selectivity

Electrochim. Acta 2022, 403, 139714; ACS Appl. Energ. Mater. 2024, 7, 1802-1813

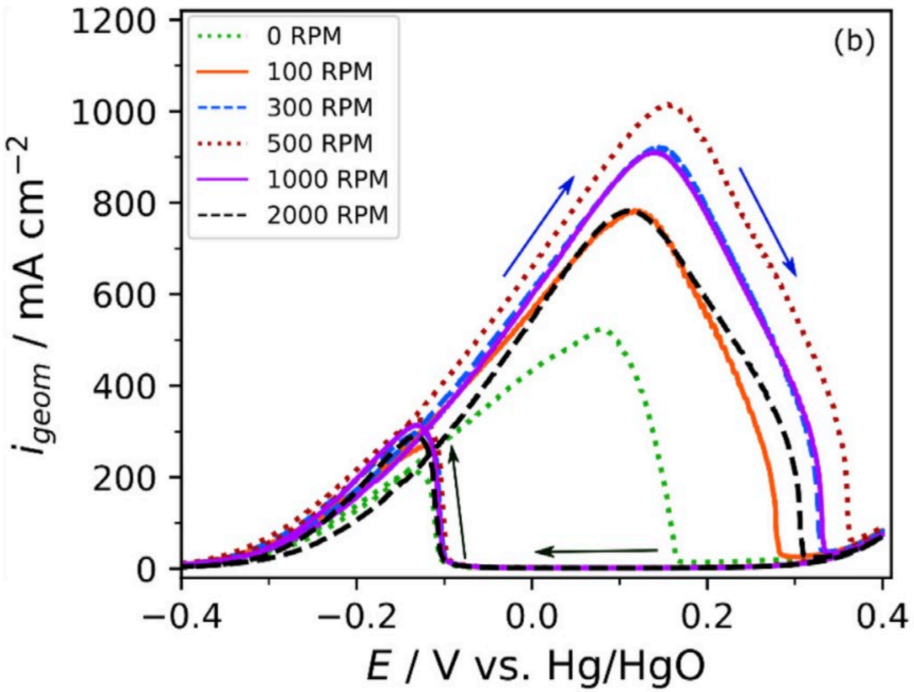
Factors controlling activity in BiORs

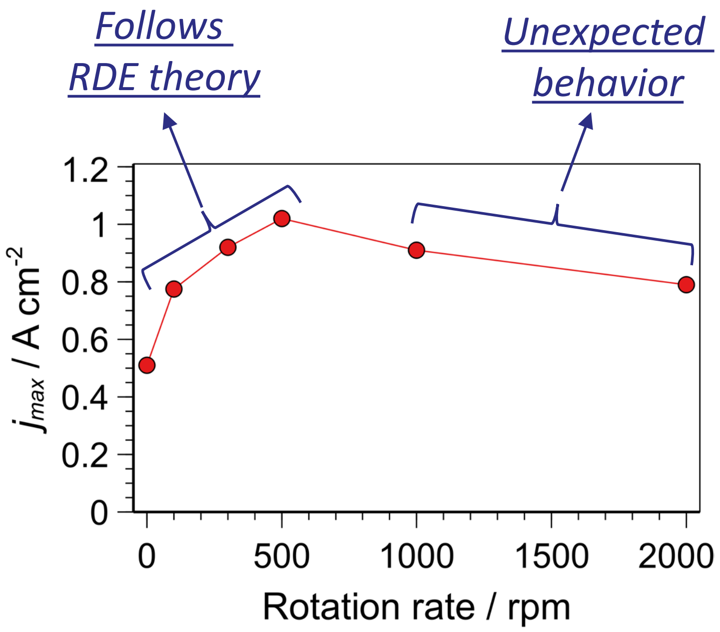
Mass transport

Rotating disk electrode (RDE) to control mass transport rates



Glycerol oxidation; PdNi, 25 °C





✔ **Medium mass transport rates**

✘ **j_{max} decreases at high rates**

Caused by reaction pathways to different oxidation products

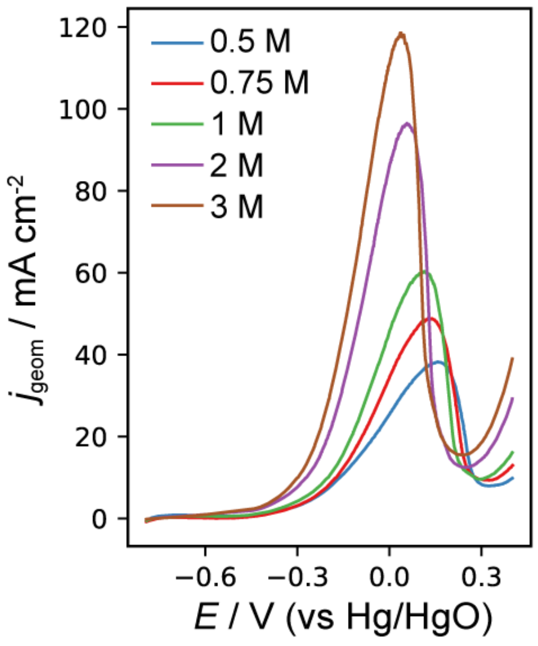
Optimal mass transport depends on BiOR reactant, catalyst morphology, pH, etc.

ChemSusChem 2021, 14 (8), 1902–1912; Electrochim. Acta 2022, 403, 139714; Int. J. Hydrogen Energy 2021, 46, 1615-1626

Factors controlling activity in BiORs

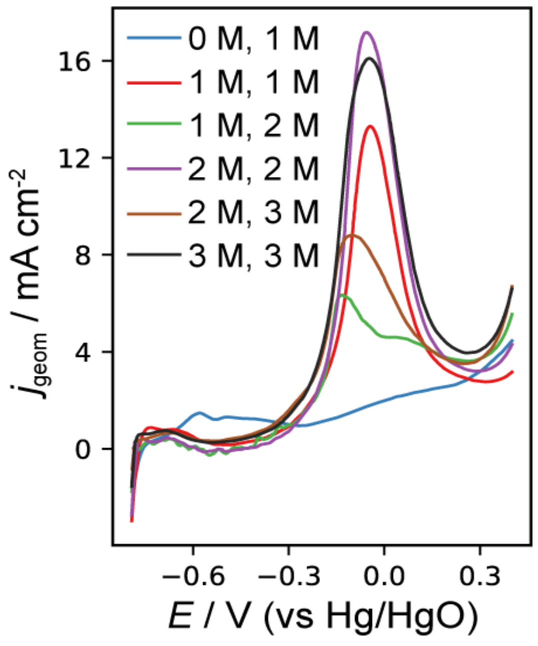
pH effect

0.5 M GA in [NaOH]



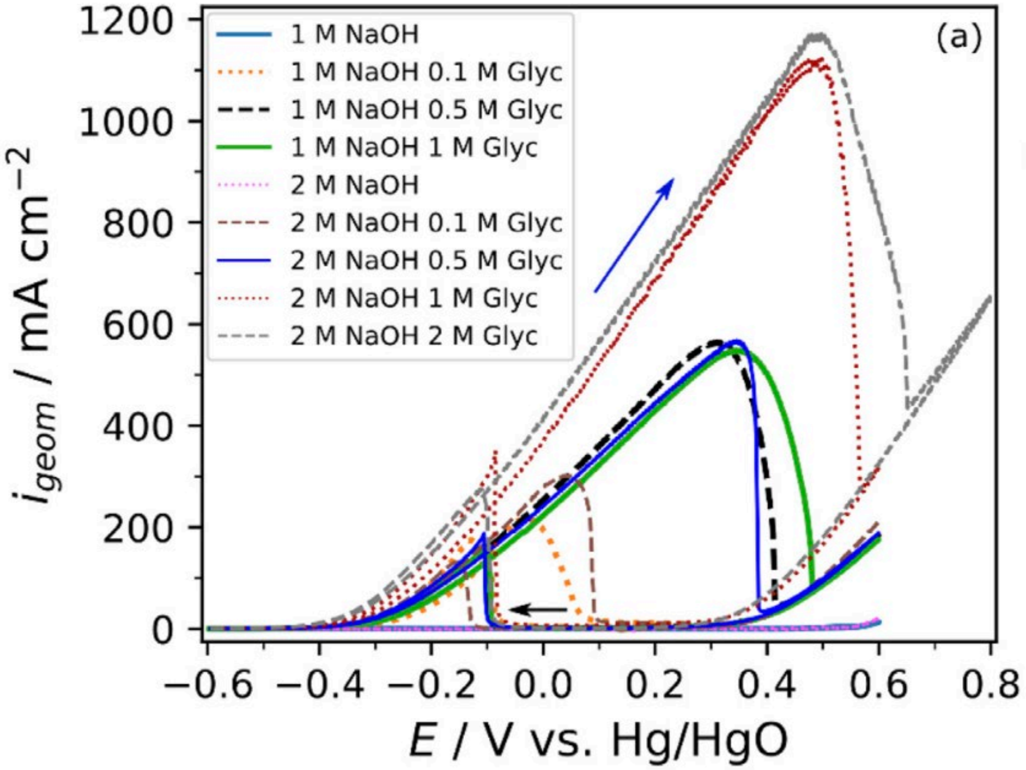
- **Higher pH → Higher j_{max}**
- **OH^- strongly involved**

[LA] in [NaOH]



- ***Higher* pH → Lower j_{max}**
- **Excess OH^- block catalytic sites**

[Glycerol] in [NaOH]



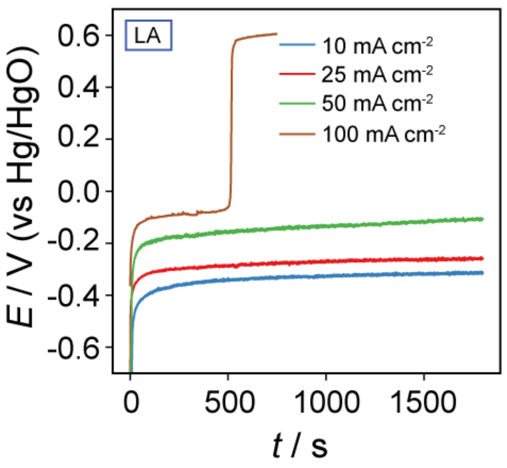
- ***Optimal 2:1 ratio [NaOH]:[Glycerol]***

ChemSusChem 2021, 14 (8), 1902–1912; Electrochim. Acta 2022, 403, 139714

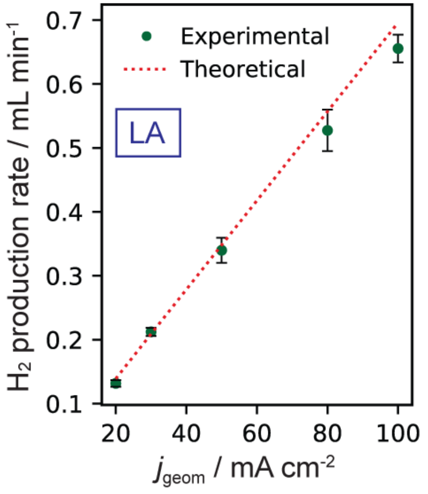
Relevance of activity in co-electrolysis for H_2 production

Maximum j supporting BiOR at low potentials

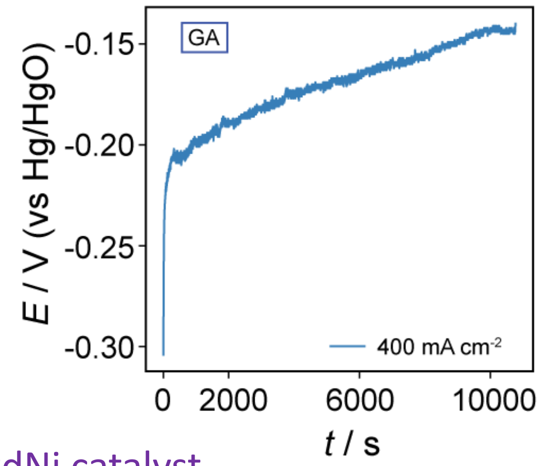
2 M LA in 2 M NaOH; 80 °C

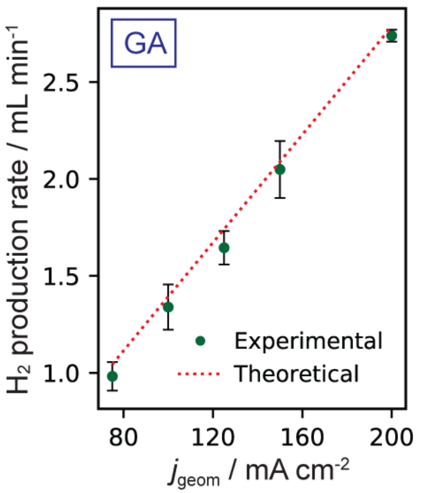


~100% H_2 Faradaic efficiency
(membrane-free cell)



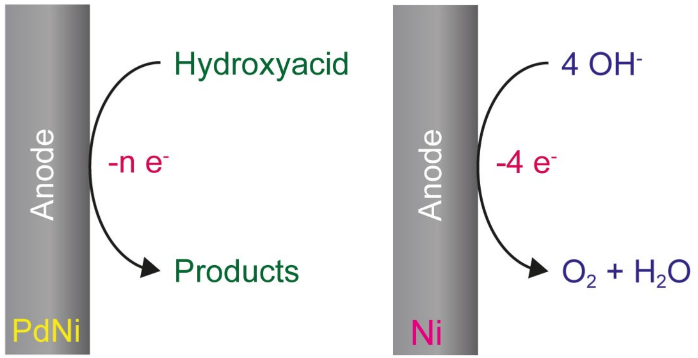
0.5 M GA in 3 M NaOH; 80 °C

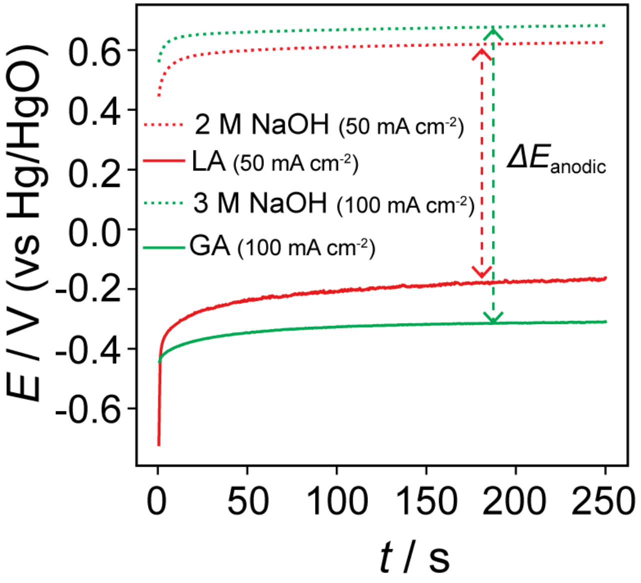




PdNi catalyst

Energy savings BiOR vs OER





ΔE_{anodic}
LA: 0.80 V
GA: 0.99 V

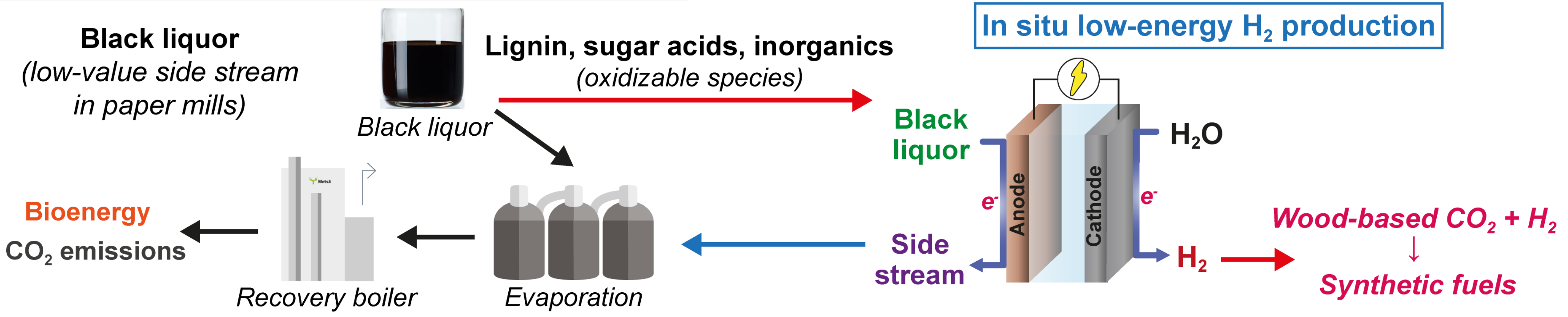
LA at 50 mA cm^{-2} → 21.2 kWh kg^{-1} H_2 less

GA at 100 mA cm^{-2} → 26.3 kWh kg^{-1} H_2 less

ChemSusChem 2021, 14 (8), 1902–1912

Co-electrolysis with industrial side streams

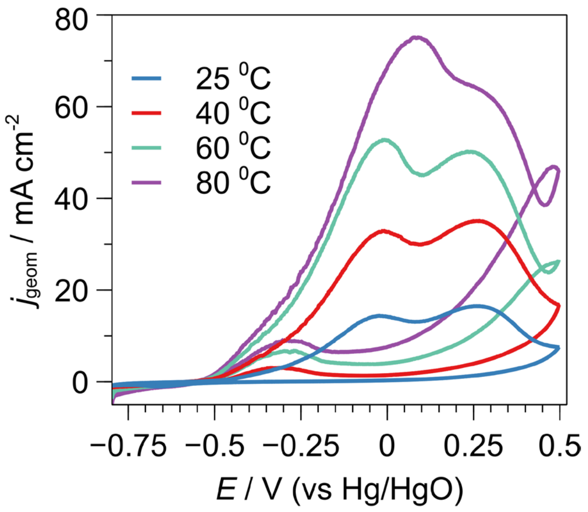
Focus on co-electrolysis for H_2 production



Electro-oxidation of Black Liquor

Noble-metal catalysts

PdNi

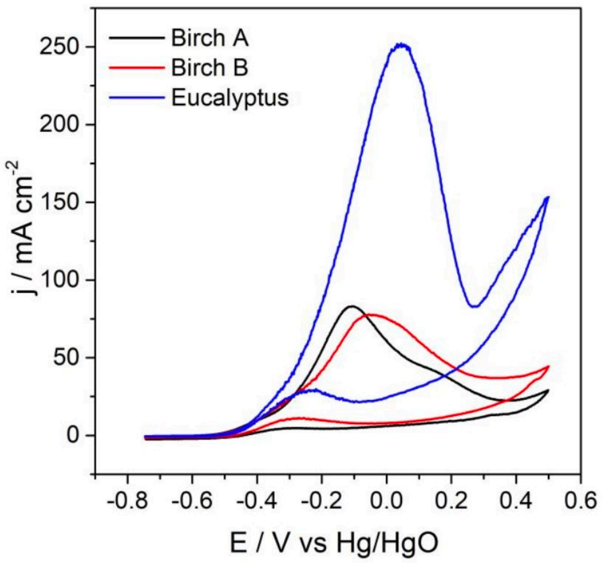


Inexpensive catalysts

NiO_x/Ni

Similar activity than PdNi

BL feedstock effect

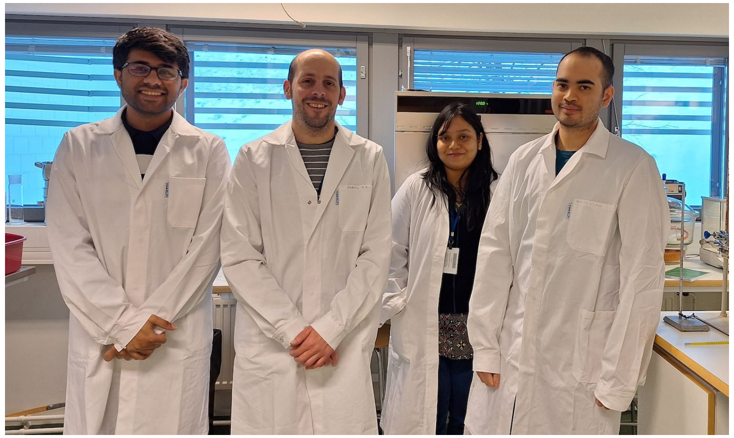


Black liquor in 3 M NaOH

Preliminary results

Acknowledgements

Nanoelectrochemical Discovery Group



Incoming 2025!

Aalto University

Electrochemical Materials and Applications
Research Group

ACADEMY OF FINLAND

NordForsk

Collaborators:

KTH VETENSKAP OCH KONST

Dr. Jai White
Prof. Ann Cornell
Prof. Gunnar Henriksson

Stockholm University

Swedish Energy Agency

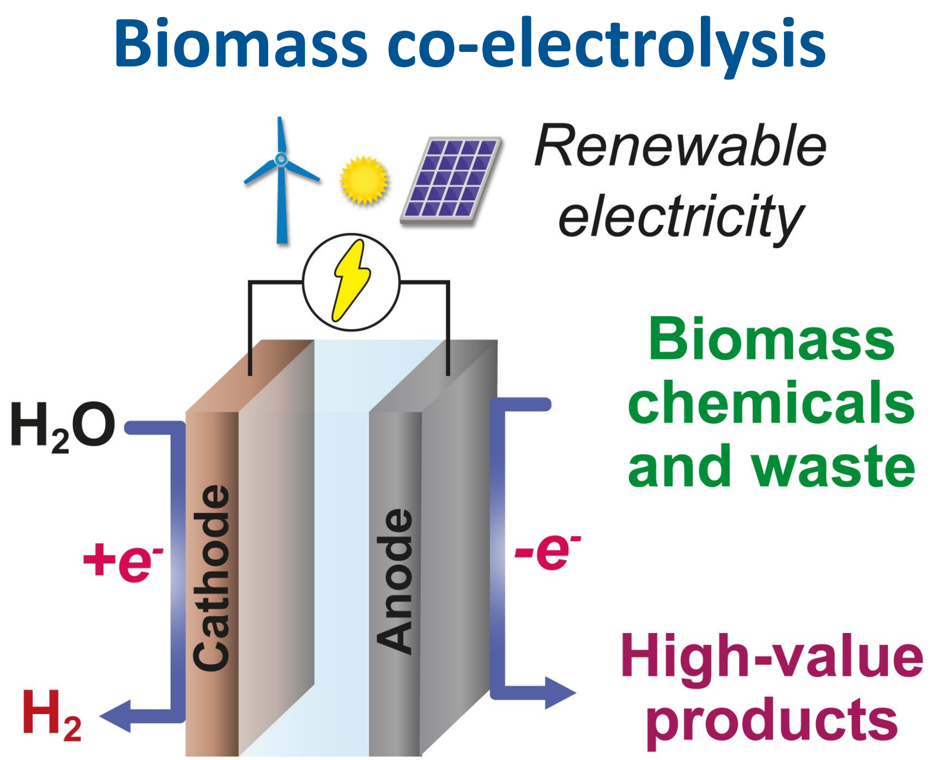
SUSTAINABLE DEVELOPMENT GOALS

7 AFFORDABLE AND CLEAN ENERGY

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

13 CLIMATE ACTION

Biomass co-electrolysis: take home messages



Potential contributions:

- Green H_2 production with low energy consumption
- Circular economy: electro-valorization of biomass waste
- Net-zero sustainable production of carbon chemicals
- Finland’s R&D ecosystem: Hydrogen and Bio Economies

Scientific challenges (*focus on electrocatalysis*):

- Highly active but affordable electrocatalytic materials
- Reaction selectivity to maximize economic impact
- Raw feedstocks: understanding role of impurities
- Tailored materials and conditions for each feedstock