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ELECTROCHEMICAL PROCESS DEVELOPMENT FOR MALEIC ACID PRODUCTION

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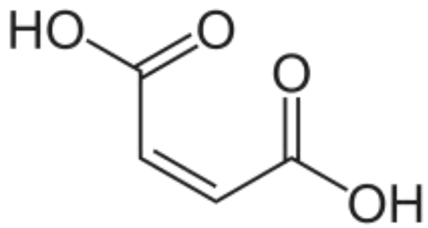
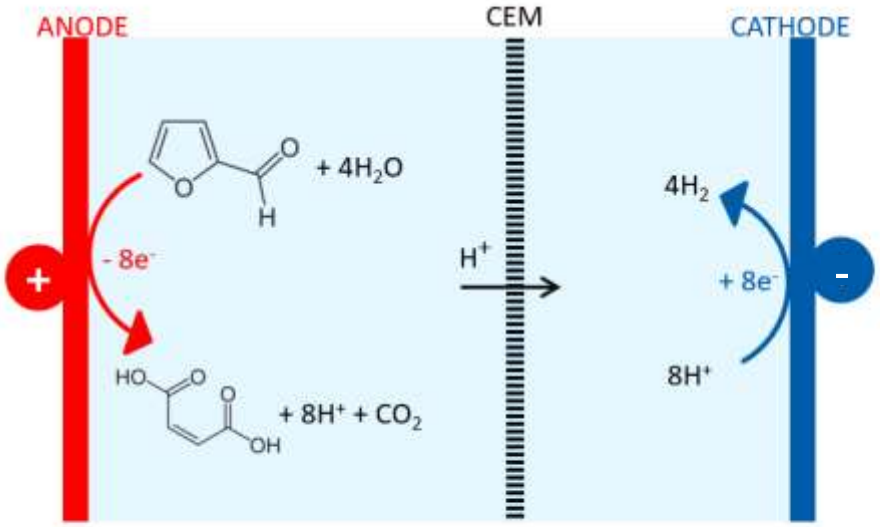
MOTIVATION & OBJECTIVE
BIO-BASED MALEIC ACID PRODUCTION



Maleic acid/anhydride:

- Available only from fossil based feedstocks, butane or benzene
- Applications: polymers (incl. biodegradable), lubricants, plasticizers, bio-aromatics
- Electrochemical production can offer “green” conversion based on renewable feedstock and energy

MALEIC ACID PRODUCTION VIA ELECTROLYSIS
REACTION MECHANISMS

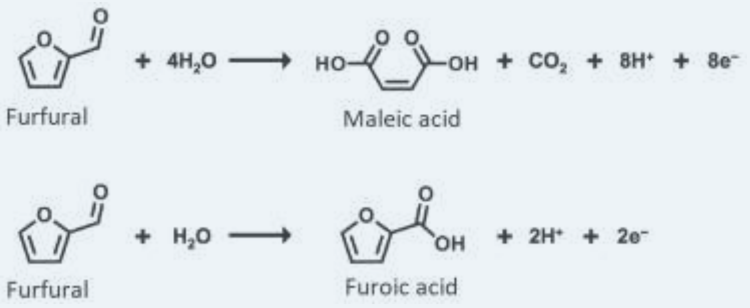


(-)	$8H^+ + 8e \longrightarrow 4H_2$
(+)	FF ($C_5H_4O_2$) + $4H_2O \longrightarrow$ MA ($C_4H_4O_4$) + CO_2 + $8H^+$
Overall:	FF ($C_5H_4O_2$) + $4H_2O \longrightarrow$ MA ($C_4H_4O_4$) + CO_2 + $4H_2$

pH effect:

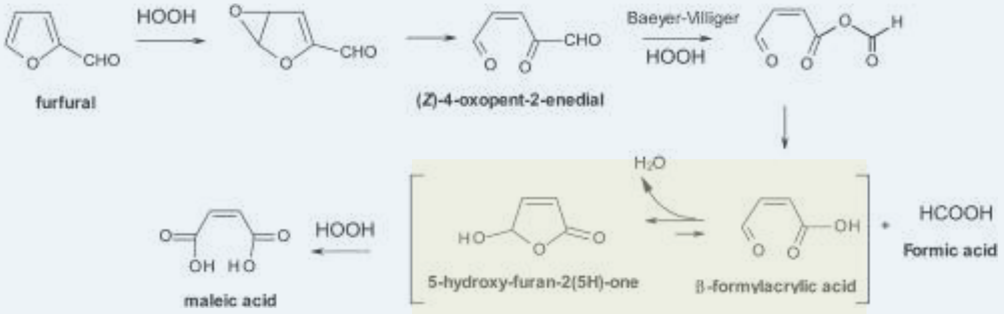
Acid:

Alkaline:



S. R. Kubota, et al, ACS Sustainable Chem. Eng.2018689596-9600

Mechanism:



N Alonso-Fagundez et al ., (2014) *RSC Advances*, 4 (98):54960–54972, 2014.

SCALE UP APPROACH

Literature study and expert opinion → Electrochemical systems

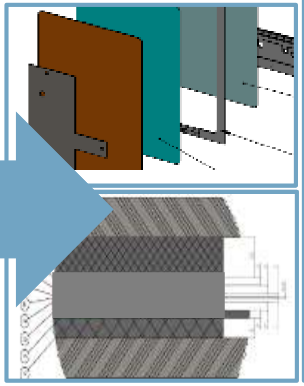
Downstream processing ⇅ Techno-economic evaluation ⇅

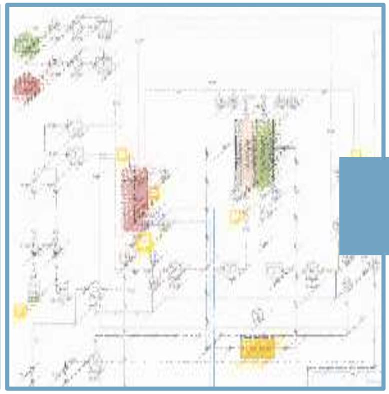
Electrochemical systems → Design of electrochemical process and development
TRL 1-2 to TRL 6 → **System integration, pilot construction & demonstration**

1. Reaction and catalyst development

1-100 cm² – 1-2 g/h

2. Reactor and process development





1000 cm² – 25-50 g/h

3. Demonstration of integrated process

1 m² – 250 g/h

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CATALYST SELECTION
CV MEASUREMENTS

- Pt & PbO_2 tested, PbO_2 – x20 higher current density, cheaper non-noble catalyst
- Furfural and furoic acid readily oxidized at 2.1 V vs RHE
- CVs indicate stability of maleic acid on PbO_2

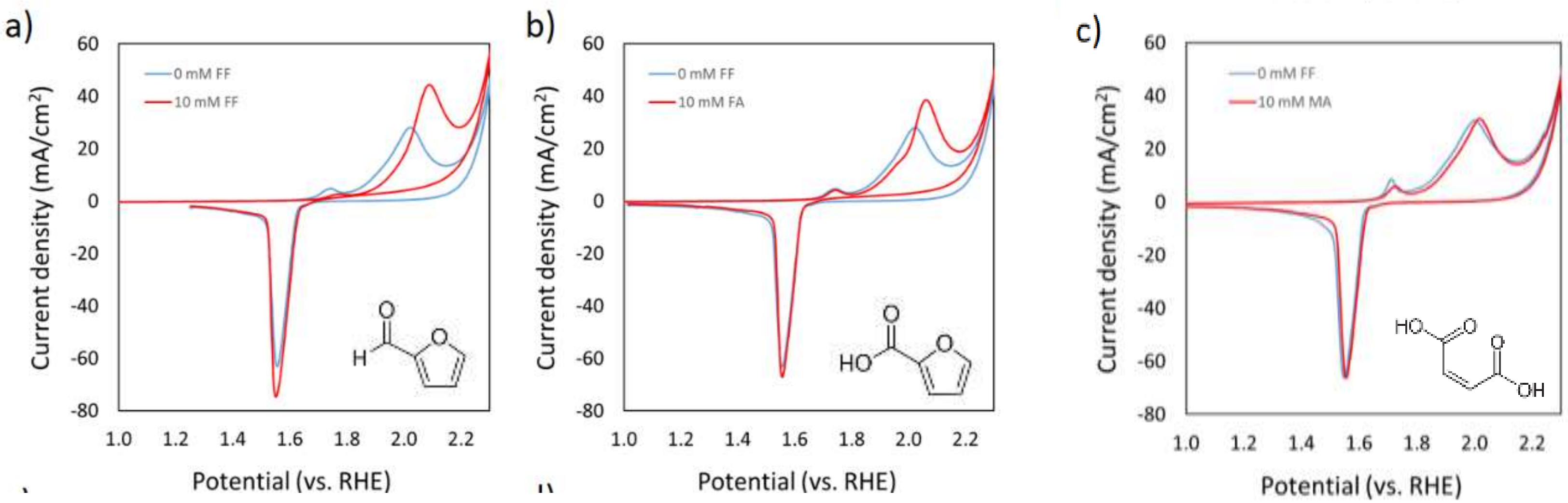
- PbO_2, cheap industrially used electrode material
- Preparation by potential cycling, 1.1 – 2.0V, till stable CV

$$PbO\cdot(OH)_2 + H_2O \rightarrow PbO\cdot(OH)_2 \ldots (OH^{\bullet}) + H^+ + e^-, \quad (1)$$

$$PbO\cdot(OH)_2 \ldots (OH^{\bullet}) \rightarrow PbO\cdot(OH)_2 + O + H^+ + e^-, \quad (2)$$

$$2\,O \rightarrow O_2. \quad (3)$$

$$2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2\,e- \quad (4)$$

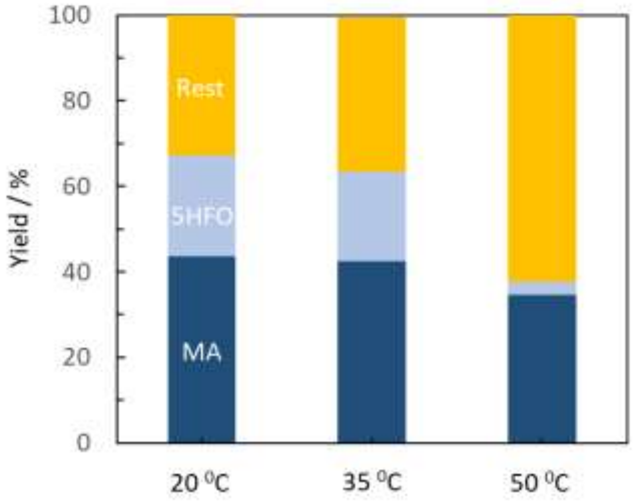


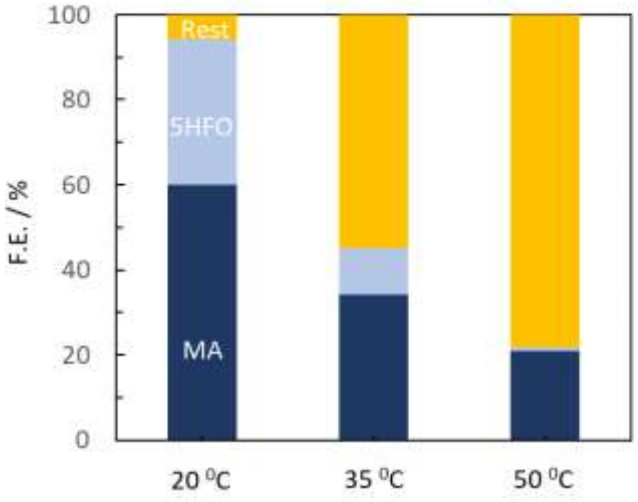
ELECTROLYSIS OPTIMIZATION

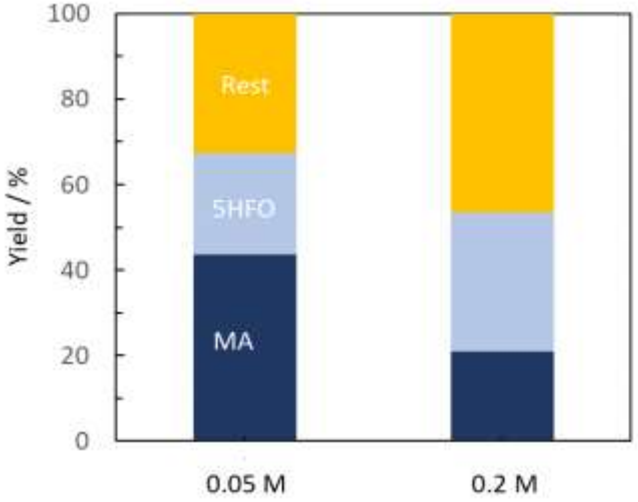
Electrolysis 50 mM Furfural on PbO_2: ~70% yield MA + 5HFO, FE~ 80%

- Feedstock: Maleic acid formed by electrolysis of furfural, furoic acid, 5HFO
- Electrode material: DSA, BDD, Pb alloys, PbO_2. Latter shows best activity.
- Residence time: Longer residence time, lower yield
- Temperature: Increase of temperature, lower efficiency, higher product degradation, higher current density (20-60 mA/cm^2)

Electrolysis conditions: Oxidation of 50 mM FF , fixed potential (1.85 V vs SCE) on a PbO_2 (10 cm2) anode as WE, Pt CE and SCE as RE in a 1M H2SO4, 7 hours.

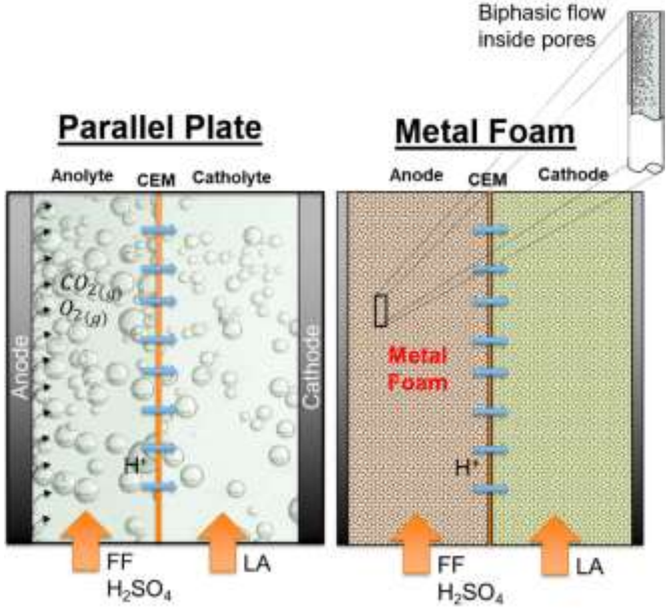


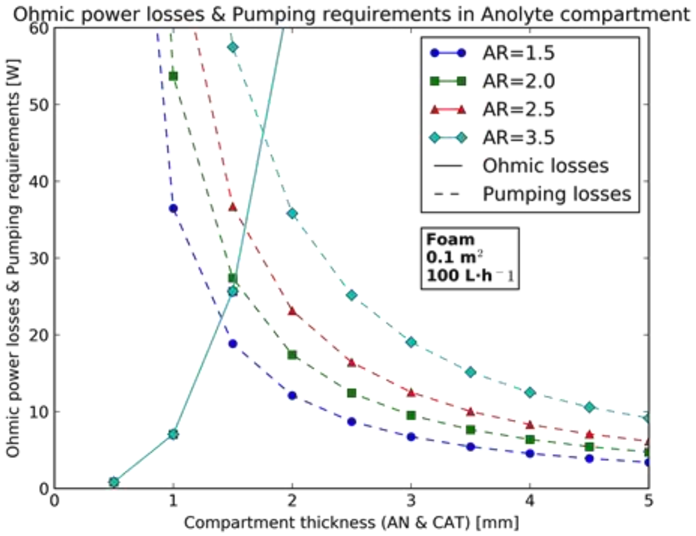


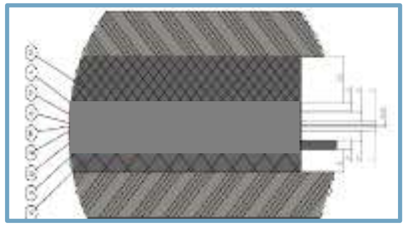


REACTOR SCALE UP
10-100 CM² → 1000 CM²

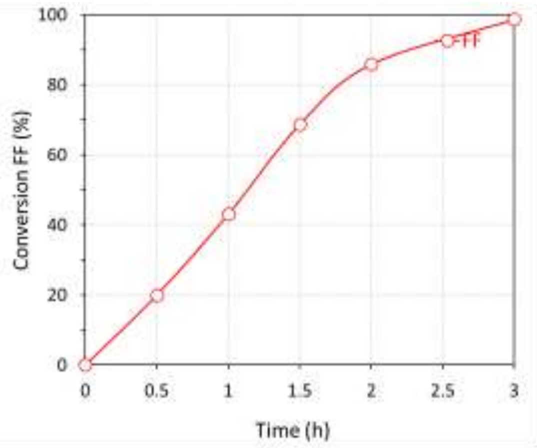
- Reactor development
  - Performance and materials requirements → specifications
  - Reactor modelling
  - Construction of a flexible reactor (flexible interelectrode distance, electrode type)
  - Optimization of reactor performance (CD, FE, Cell voltage)
    - Flow and reactor configuration
    - Electrolysis mode, feed dosing

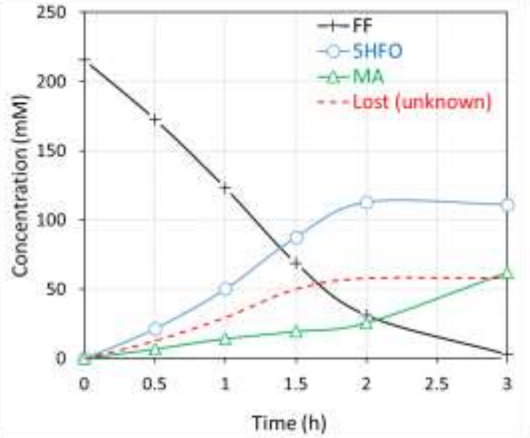


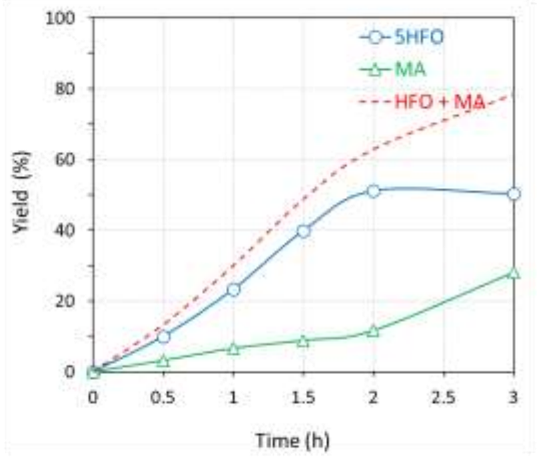


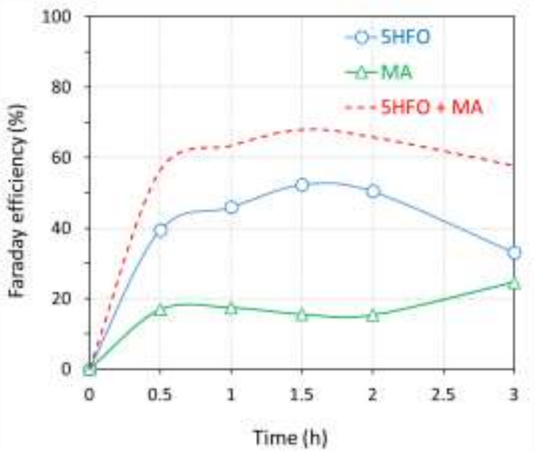


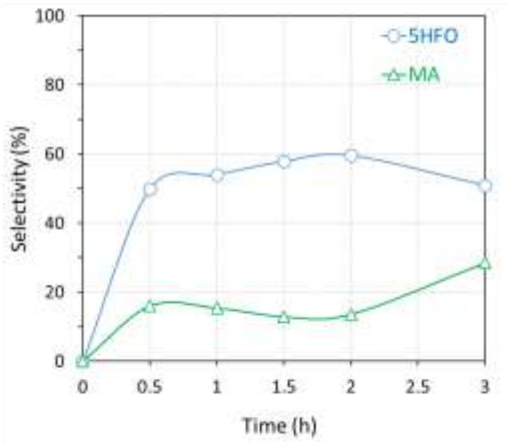
MALEIC ACID PRODUCTION
ELECTROLYSIS PERFORMANCE











- 99% FF conversion
- 80% combined yield of HFO and MA
- Selectivity: HFO ~60%, MA ~30%
- Overall F.E. ~70%
- Main losses of FF within 1.5 hrs, then stable
- Longer electrolysis is required!
- Main challenges:
  - Selectivity & FE
  - Stability of Pb electrodes (~0.005 mg/cm^2*hr → ~0.4 kg/m^2*year)
  - Reactant crossover
  - Gas management

MALEIC ACID SEPARATION
MA OBTAINED IN A PILOT SCALE 5L CRYSTALLIZER

- MA separation from reaction mixture: pre-concentration followed by cooling crystallization, filtration, washing and drying
- Crystallization step requires concentrated MA in the acidic electrolyte
- Separation yield ~85%, purity >95%
- Slight coloration observed due to furfural degradation products. Sulfuric acid content ~0.5% in final sample and 1% 5HFO.

MA crystals before; after washing after drying

Pre-concentration → Crystallization → Filtration & washing →

Maleic acid crystals

TECHNO-ECONOMIC ANALYSIS
FURFURAL TO MALEIC ANHYDRIDE

ELECTROLYSER

- MA production costs: 1.3 – 2.5 Euro/kg
- Represent 30-50% of total costs (depends on case)
- H_2 cogeneration in Cathode: associated H_2 sales discount
  - Drives down total Electrolyser Costs

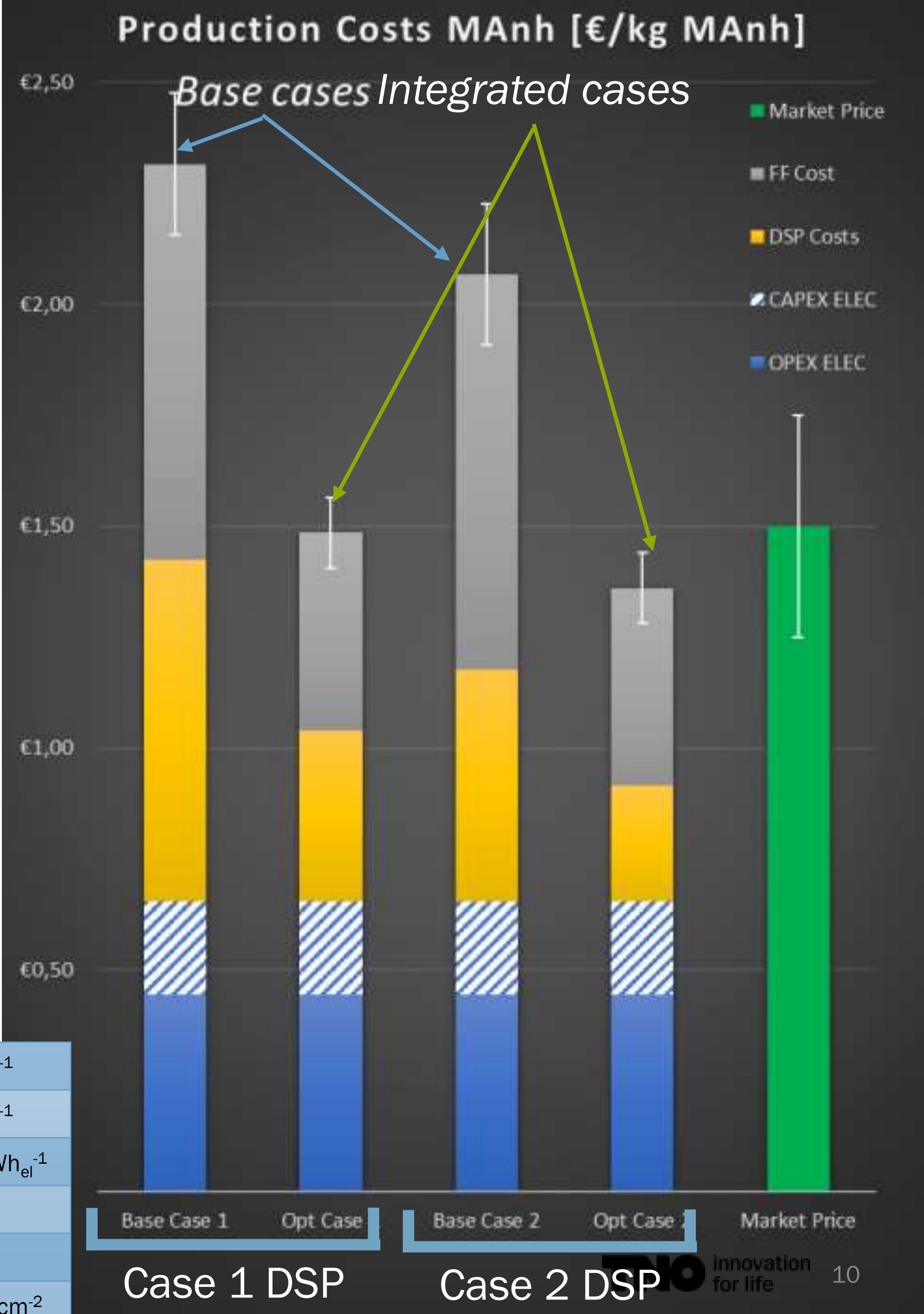
BASE CASE VS. INTEGRATED CASE

- **Base Case:**
  - FF is purchased in pure form and diluted: higher FF cost (40% of total costs)
  - DSP: Pre-concentration & dehydration vs extraction & dehydration
  - Non-optimised separation: lab-scale exp. Results to model process (25-33% of total costs)
- **Integrated case:**
  - FF can be purchased in a 10-15%wt. aq. Solution: -50% FF costs (30% total costs)
  - Integrated separation process: expected 50% cost reduction for both cases (20-25% of total costs)

POSITIVE ECONOMIC BALANCE FOR INTEGRATED CASE

- Valid for both separation Case 1 & 2
- MAnh price can range from 1,25 – 1,50 €/kg: varies with oil price

H_2 price	1,50	$€{\cdot}kg^{-1}$
O_2 price	0,05	$€{\cdot}kg^{-1}$
El. Cost	0,05	$€{\cdot}kWh_{el}^{-1}$
FE	70	%
Y	80	%
CD	300	$mA\ cm^{-2}$



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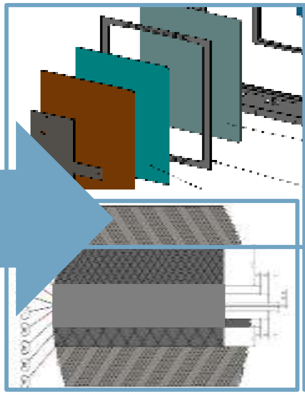
SUMMARY

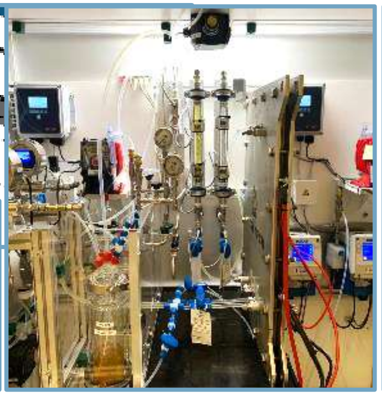
- Feasible electrochemical production of bio-based maleic acid from furfural
- Scaled up from few cm^2 to 1000 cm^2 continuous flow electrolysis unit
  - MA yield ~30%, 5HFO yield ~50% (combined yield ~80%), overall F.E. ~70%
  - Next, electrolysis with porous electrodes and stacked cell testing of 1 m^2
- MA Separation yield ~85, purity >95%
- Potentially positive business case, production costs 1.3 – 2.5 Euro/kg MA (market price ~ 1.5 Euro/kg)

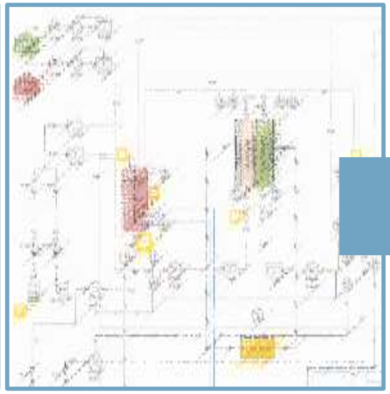
1. Reaction and catalyst development

2. Reactor and process development

1-100 cm^2 – 1-2 g/h







1000 cm^2 – 25-50 g/h

1 m^2 – 250 g/h

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THANK YOU FOR YOUR TIME

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