Continuous Process Intensification

Electrochemical Syntheses

Syntheses without Reagents

Anil Kumar

GenZ Materials

Continuous Process Intensification

Electro Organic Chemistry

Use of Electrons (Current) for Organic Synthesis

Electro Organic Chemistry

Use of Electrons (Current) for Organic Synthesis

Electrochemistry and Organic Synthesis

Electro Organic Chemistry

Use of Electrons (Current) for Organic Synthesis

Electrochemistry and Organic Synthesis

Electrochemistry  **Organic Synthesis**

Electro Organic Chemistry

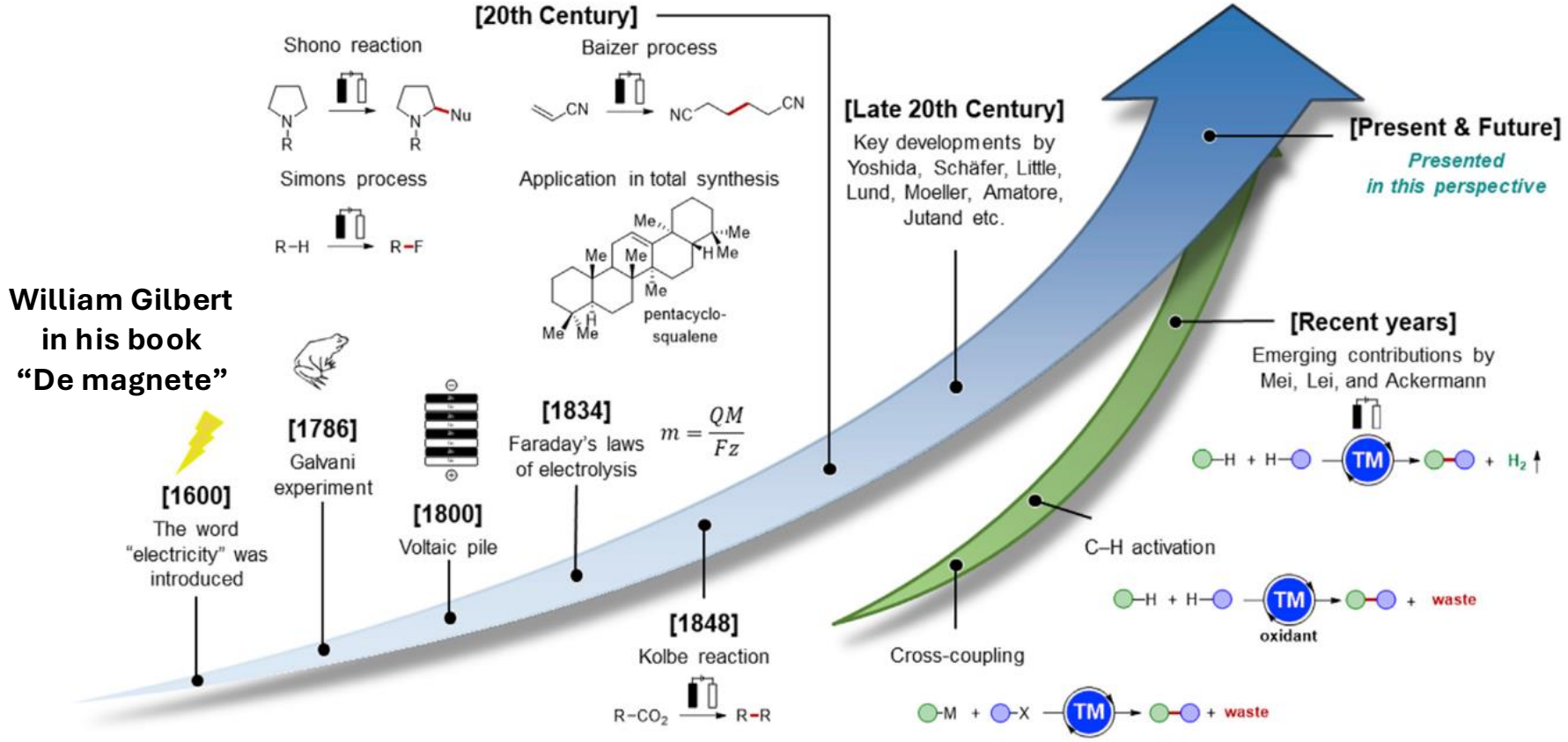
Electrochemistry **It is everywhere in daily life**

➢ Photosynthesis	Reduction
➢ Fire	Oxidation
➢ Food Digestion	Oxidation
➢ Corrosion	Oxidation
➢ Apple turning brown	Oxidation
➢ Bleaching Hair	Oxidation
➢ Electroplating	Reduction
➢ Wearable Electronics	Redox
➢ Battery, EV, PV, TV..	Redox

Electro Organic Chemistry

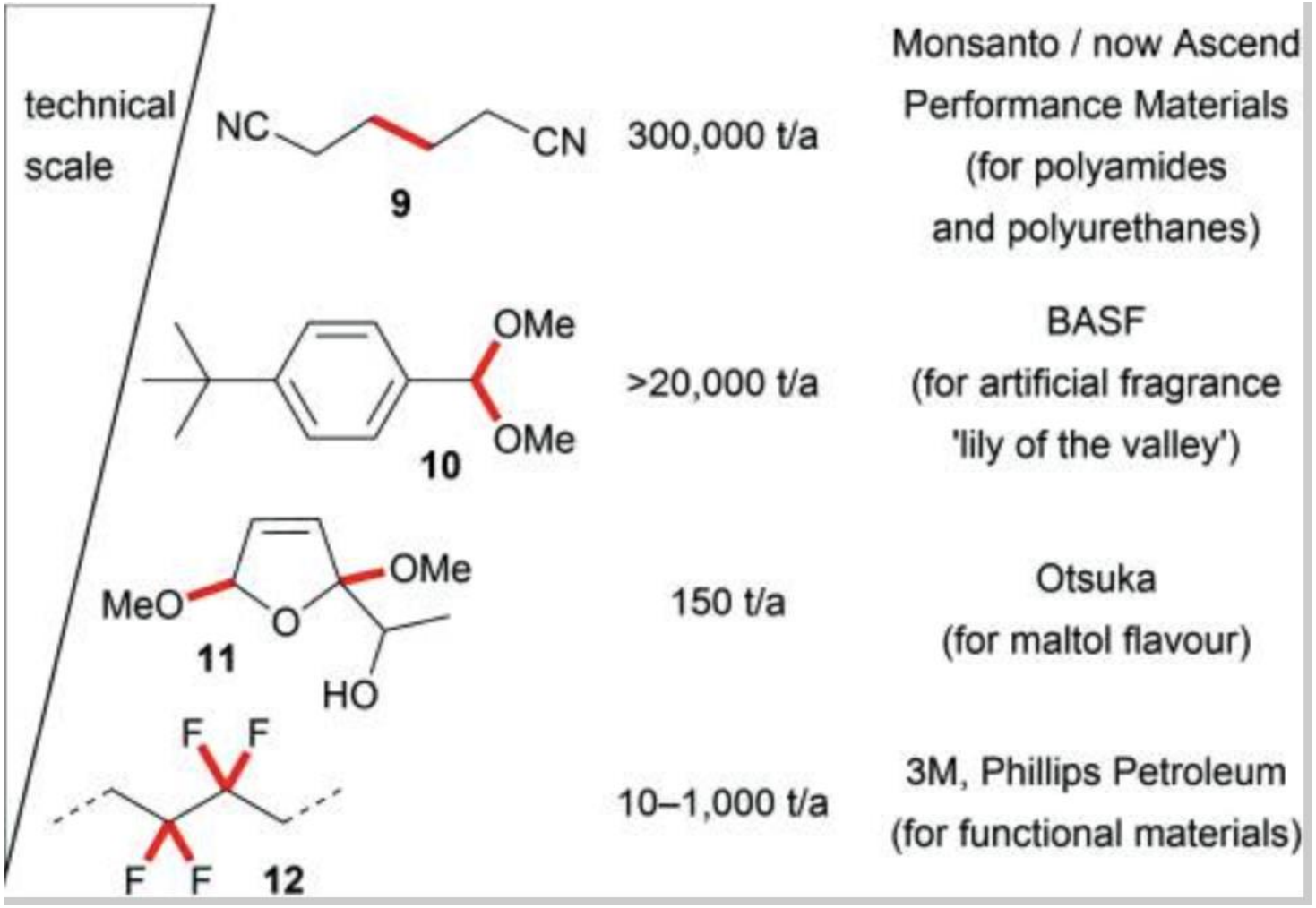
Electrochemistry was born as a synthetic chemistry

Faraday, Kolbe, Haber, among others



Ackermann and coworkers, Chem 6, 2484–2496, October 8, 2020

Electro Organic Chemistry



Continuous Flow Electrochemistry

Chem Sci. 2020 Dec 14; 11(46): 12386–12400

Electro Organic Chemistry

Why Electro Organic Chemistry now?

Electro Organic Chemistry

Why Electro Organic Chemistry now?

Electro Organic Batch Chemistry

3R (Rugged, Reproducible, Reduced Cost/Footprint)

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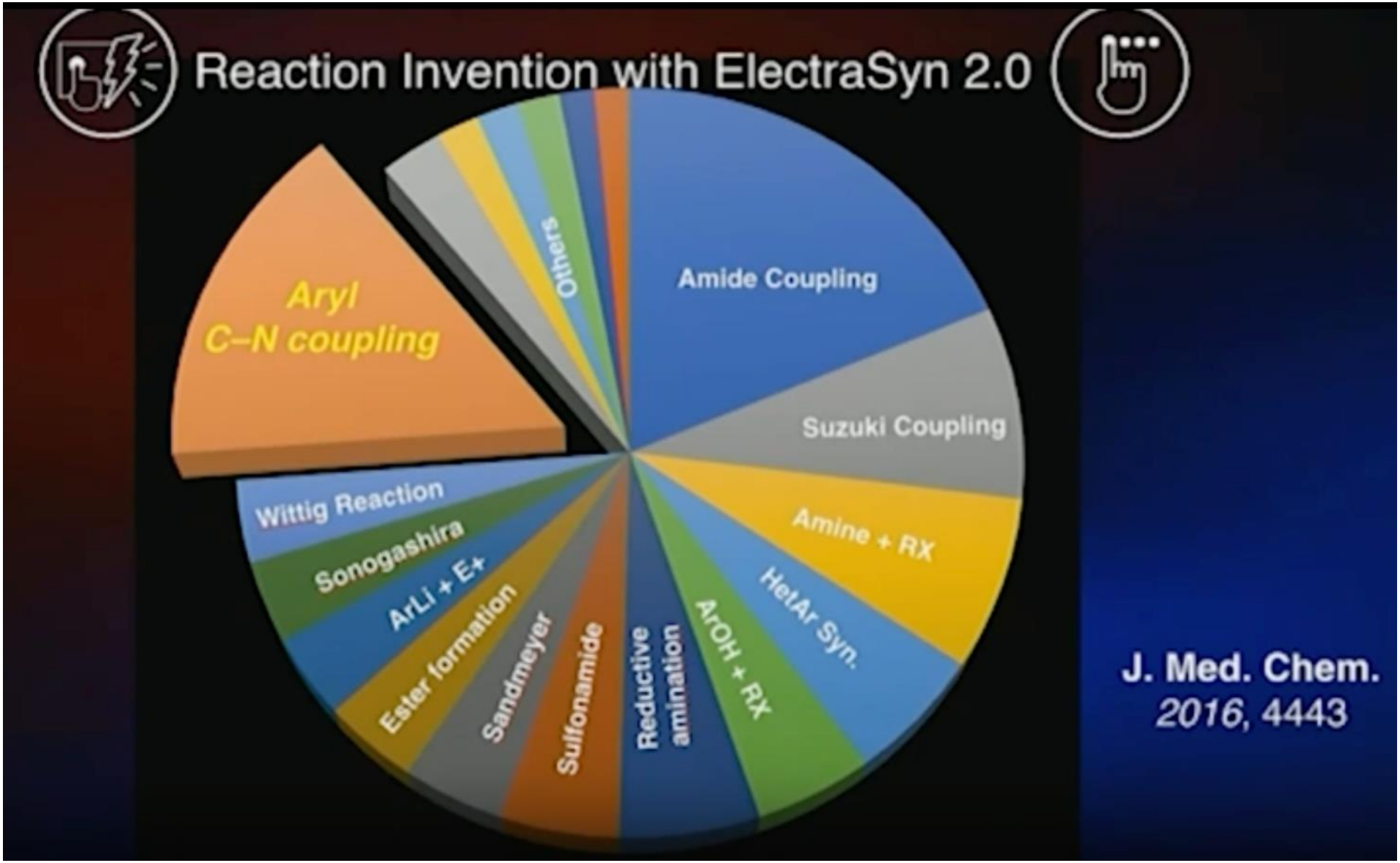
Phil Baran (https://www.scripps.edu/faculty/baran/) and IKA

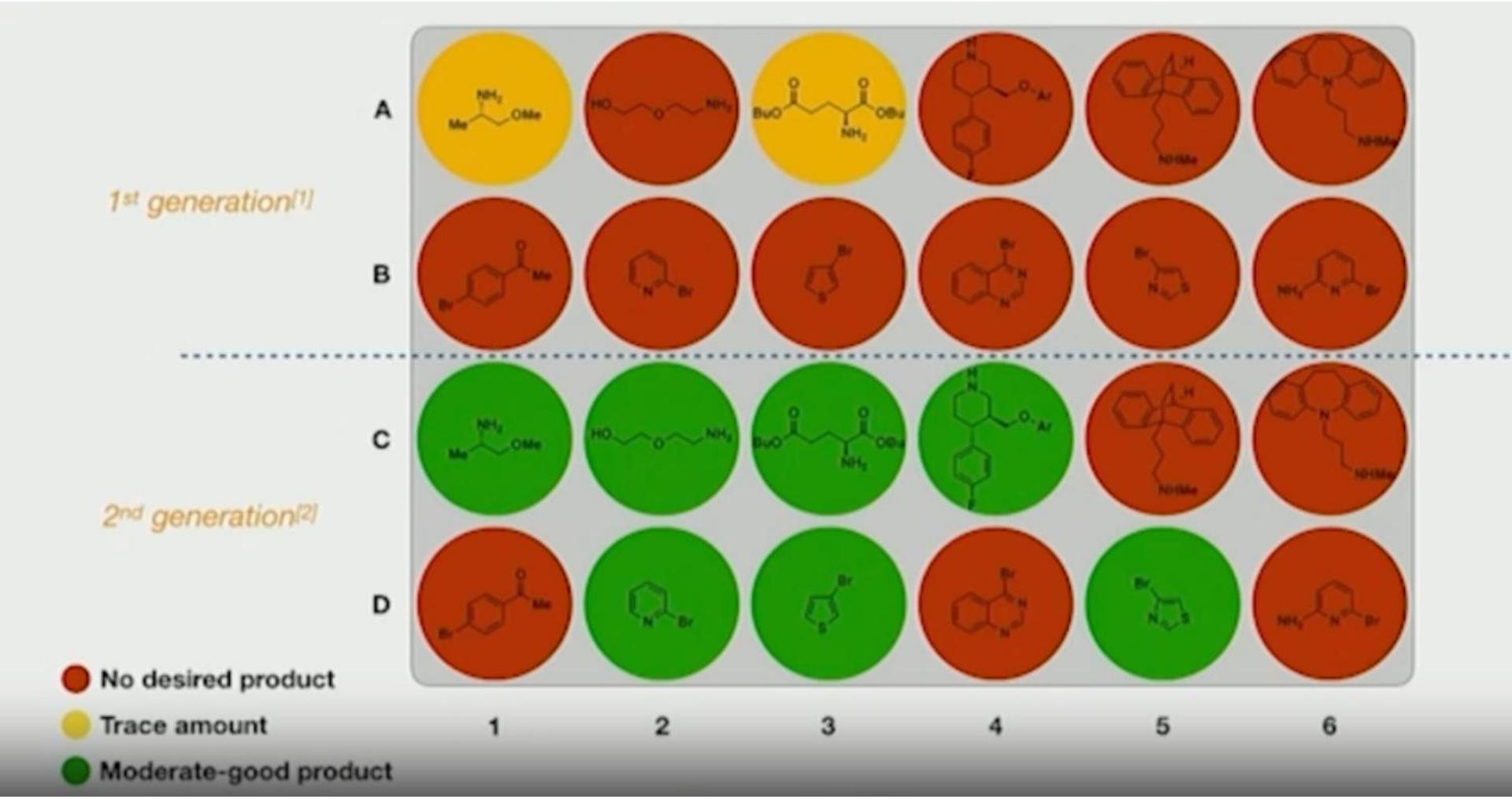
Electro Organic Chemistry

Electro Organic Chemistry



Electro Organic Chemistry

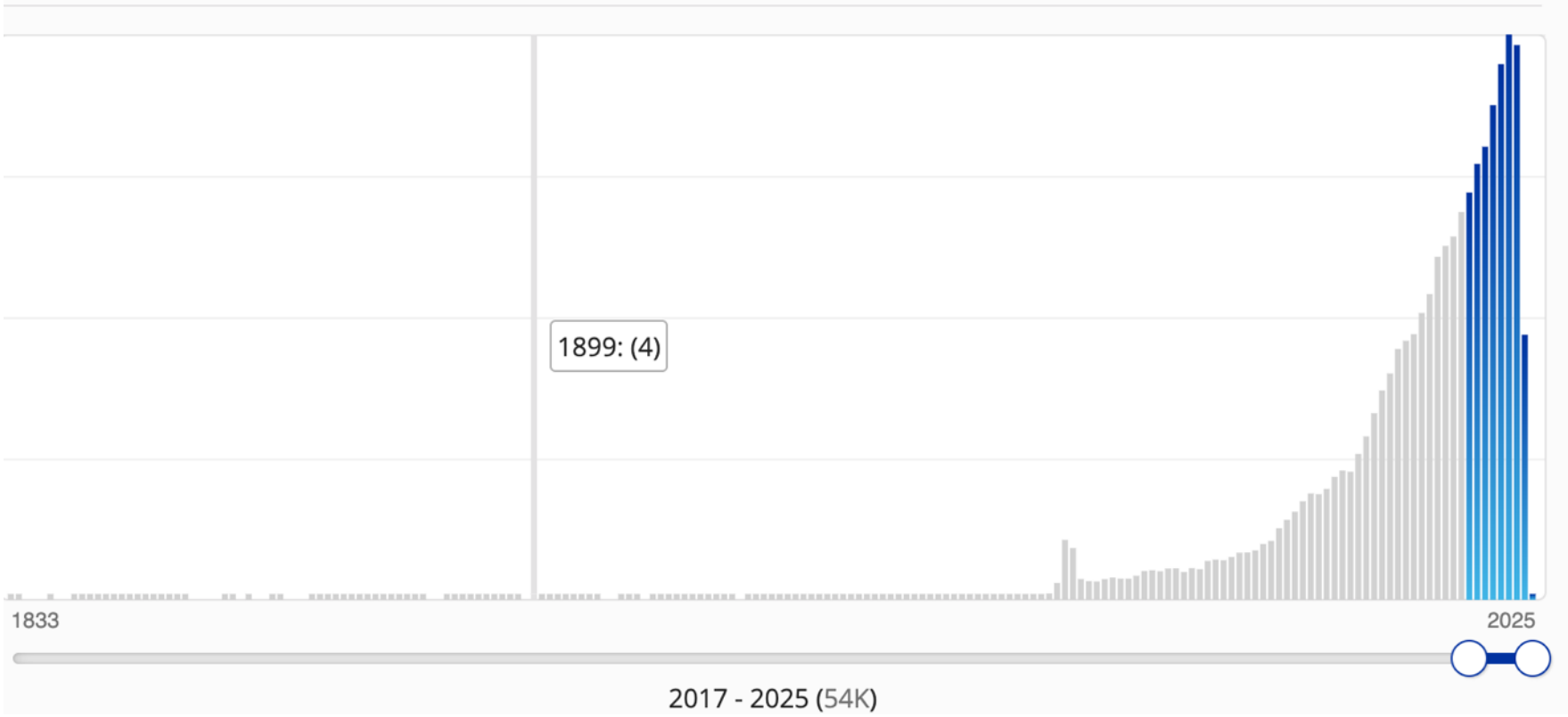
Electro Organic Chemistry



Electro Organic Lab Tools

Electrodes

Sci-Finder: Electro Organic Chemistry (23 June 2024)



Continuous Flow Chemistry Lab

Electro Organic Synthesis

LETTER

https://doi.org/10.1038/s41586-019-1539-y

Hindered dialkyl ether synthesis with electrogenerated carbocations

Jinbao Xiang[1,2,9], Ming Shang[1,9], Yu Kawamata[1], Helena Lundberg[1,3], Solomon H. Reisberg[1], Miao Chen[1], Pavel Mykhailiuk[1,4,5], Gregory Beutner[6], Michael R. Collins[7], Alyn Davies[8], Matthew Del Bel[7], Gary M. Gallego[7], Jillian E. Spangler[7], Jeremy Starr[8], Shouliang Yang[7], Donna G. Blackmond[1] & Phil S. Baran[1]*

398 | Nature | VOL 573 | 19 September 2019

SI of 447 pages

Electro Organic Chemistry

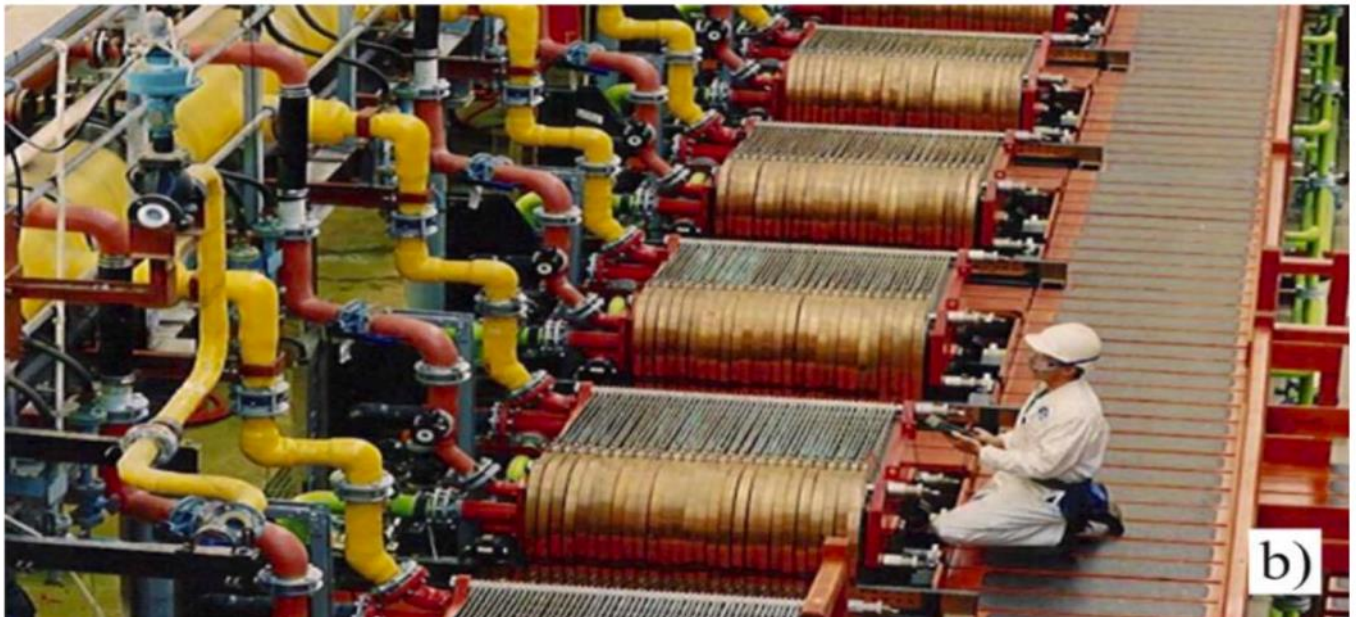
Why Electro Organic Chemistry now?

Production via Continuous Electro Flow Tools

Electro Organic Chemistry

chlor-alkali electrosynthesis

ThyssenKrupp

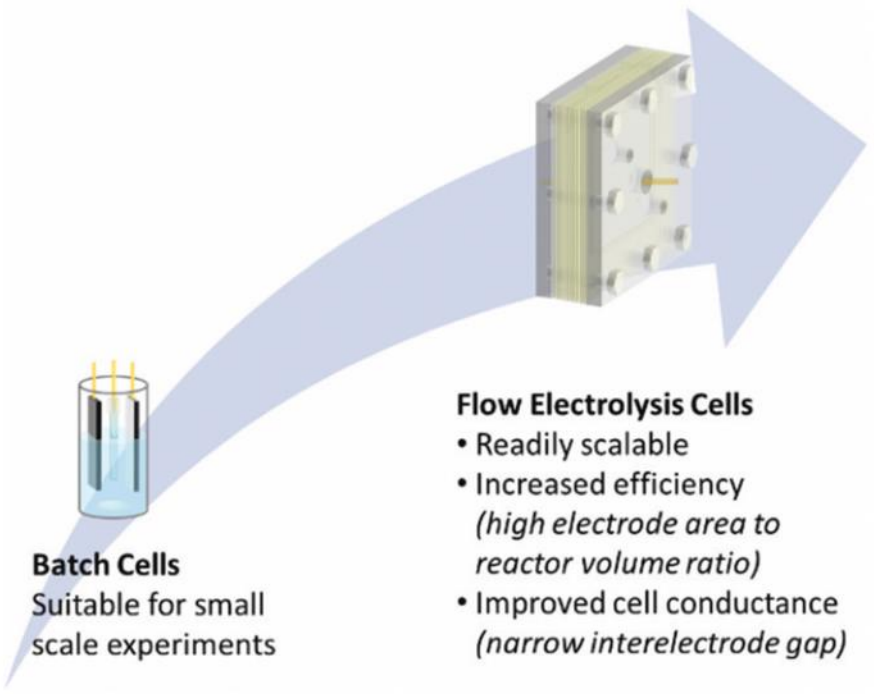


ICI Chemicals & Polymers Ltd (now Inovyn Ltd)

Electro Organic Chemistry

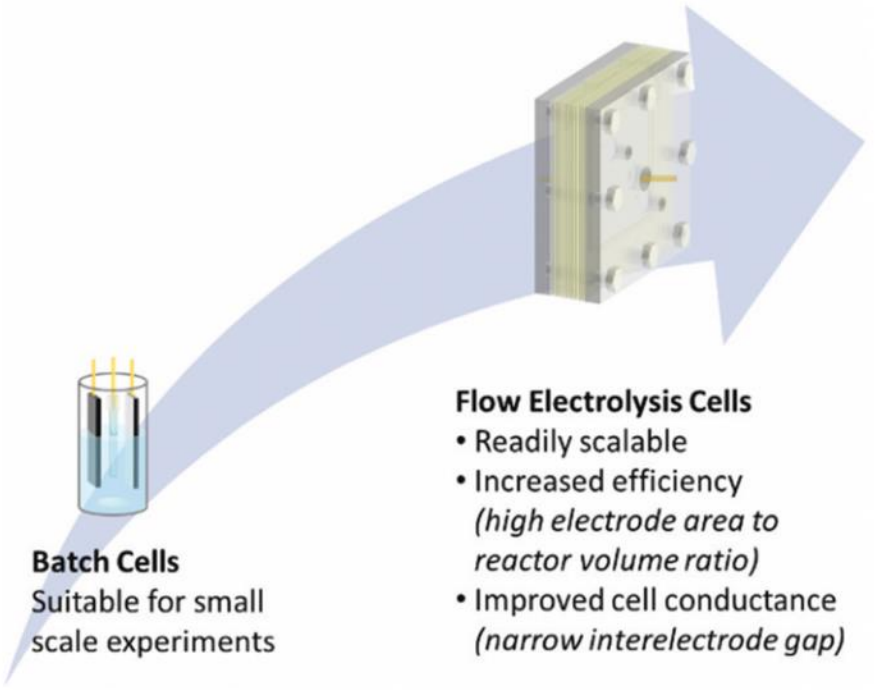
Why Electro Organic Chemistry now?

Miniaturization of Batch/Continuous Flow Tools



David Cantillo, Chem. Commun., 2022, 58, 619–628

PI Process Intensification



Most Economic Lab to Production Scale

Electro Organic Chemistry

Why Electro Organic Chemistry now?

Electro Organic Batch Chemistry

3R (Rugged, Reproducible, Reduced Cost/Footprint)

Miniaturization of Continuous Flow Tools

Electro Organic Chemistry

Why Electro Organic Chemistry now?

Electro Organic Batch Chemistry

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Miniaturization of Continuous Flow Tools

It is high time to bring back

Electrochemistry in Main Teaching Curriculum

Electro Organic Chemistry

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Miniaturization of Continuous Flow Tools

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Electrochemistry in Main Teaching Curriculum

Electrochemistry  **Organic Synthesis**

Electro Organic Chemistry

IUPAC Top Ten Emerging Technologies in Chemistry 2023

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY


Wearable sensors


Photocatalytic hydrogen


Artificial muscles


GPT language models in chemistry


Synthetic electrochemistry


Chloride-mediated removal of ocean CO_2


Phage therapy


Biological recycling of PET


Depolymerisation


"Low-sugar" vaccinations

Electro Organic Chemistry

Organic Chemist —Easier→ **Electro Organic Chemist**

Electro Chemist —not so Easy→ **Electro Organic Chemist**

Electro Organic Chemistry

What is a chemical reaction

Electro Organic Chemistry

What is a chemical reaction

Redox Reaction: A is oxidizing and B is reducing Agent

Electro Organic Chemistry

What is a chemical reaction

Redox Reaction: A is an oxidizing and B is a reducing Agent

Acid Base Reaction: A is an Acid and B is a Base

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Acid Base Reaction: A is an Acid and B is a Base

Simple Reaction: A is an electrophile and B is a nucleophile

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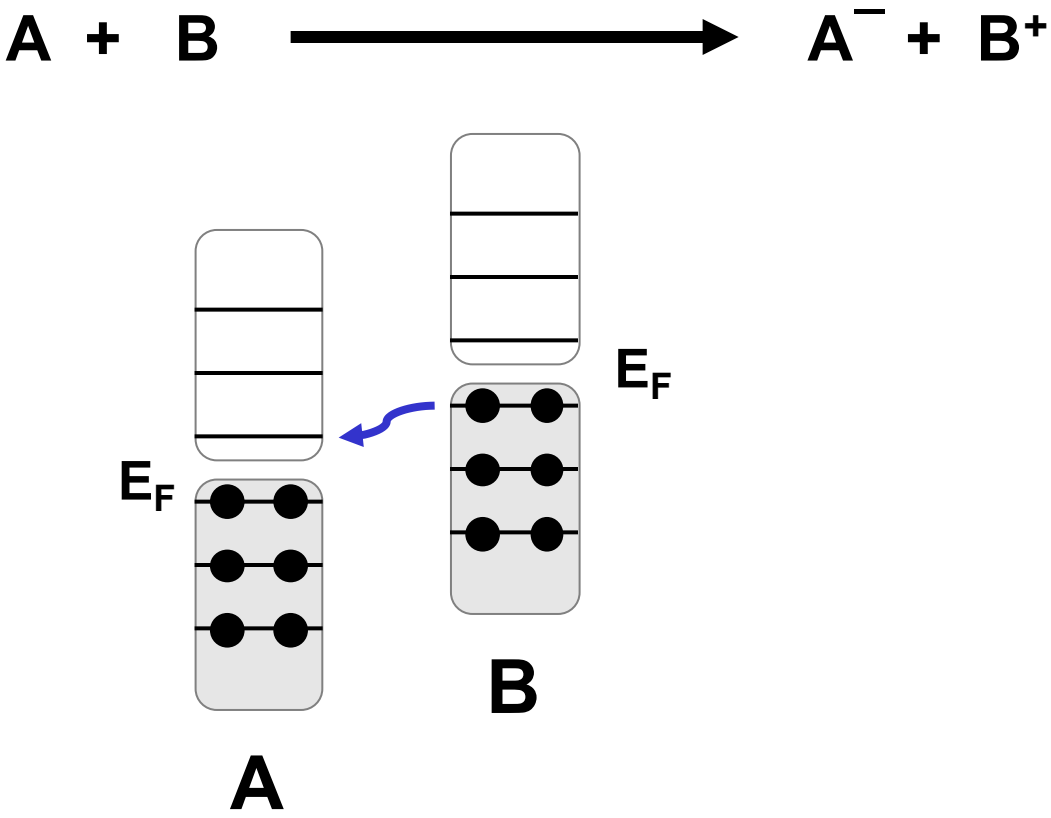
Electrons transfer from one specie (point) to another

Thermodynamics: Activation Energy, Mixing etc

Electro Organic Chemistry

What is a chemical reaction



Electrons transfer from one specie (point) to another

Thermodynamics: Activation Energy, Mixing etc

Electro Organic Synthesis

A chemical reaction is redistribution of electrons

Electrons do not care the origin: Chemical or Current

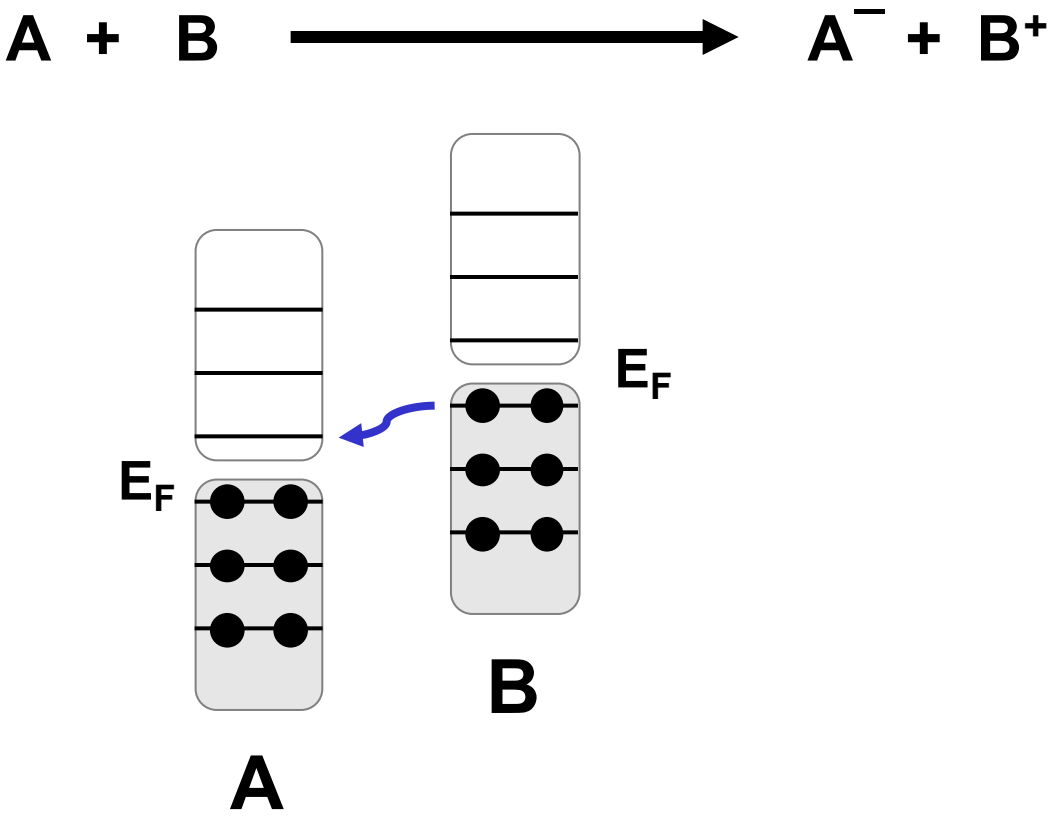
Conventional redox chemistry
- Chemical reagents utilized
- Expensive, often hazardous
- Waste generation

Electroorganic synthesis
- Electricity transforms materials
- Inexpensive, safe, renewable
- Low waste generation

David Cantillo, Chem. Commun., 2022, 58, 619–628

Electro Organic Chemistry

What is a chemical reaction

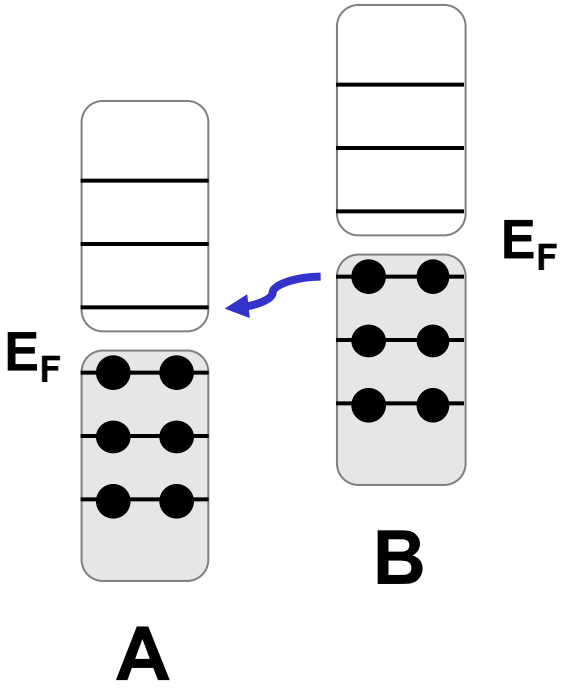


Synthetic Chemist: Nucleophilicity, Basicity, Reducing Power…

Electro Organic Chemistry

What is a chemical reaction

$$A + B \longrightarrow A^{-} + B^{+}$$



Synthetic Chemist: Nucleophilicity, Basicity, Reducing Power…

It is same as the Relative Fermi Energy Levels

Electro Organic Chemistry

Fermi Levels Control Organic Chemistry ?

Electro Organic Chemistry

Fermi Levels Control Organic Chemistry ?

Can we vary Fermi Levels externally ?

Electro Organic Chemistry

Fermi Levels Control Organic Chemistry ?

Can we vary Fermi Levels externally ?

Infinite number of synthetic reagents ?

Electro Organic Chemistry

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Electro Organic Chemistry

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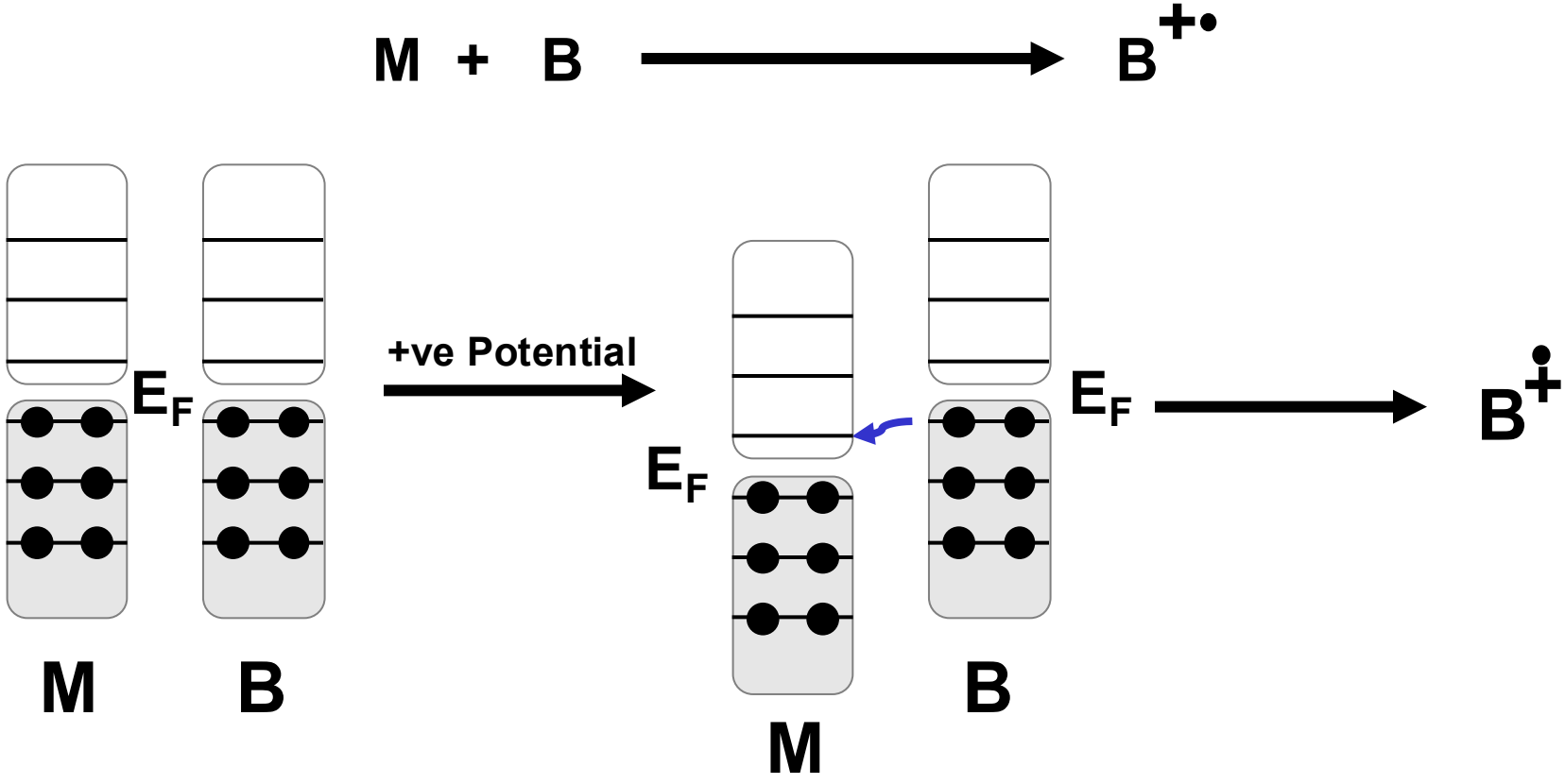
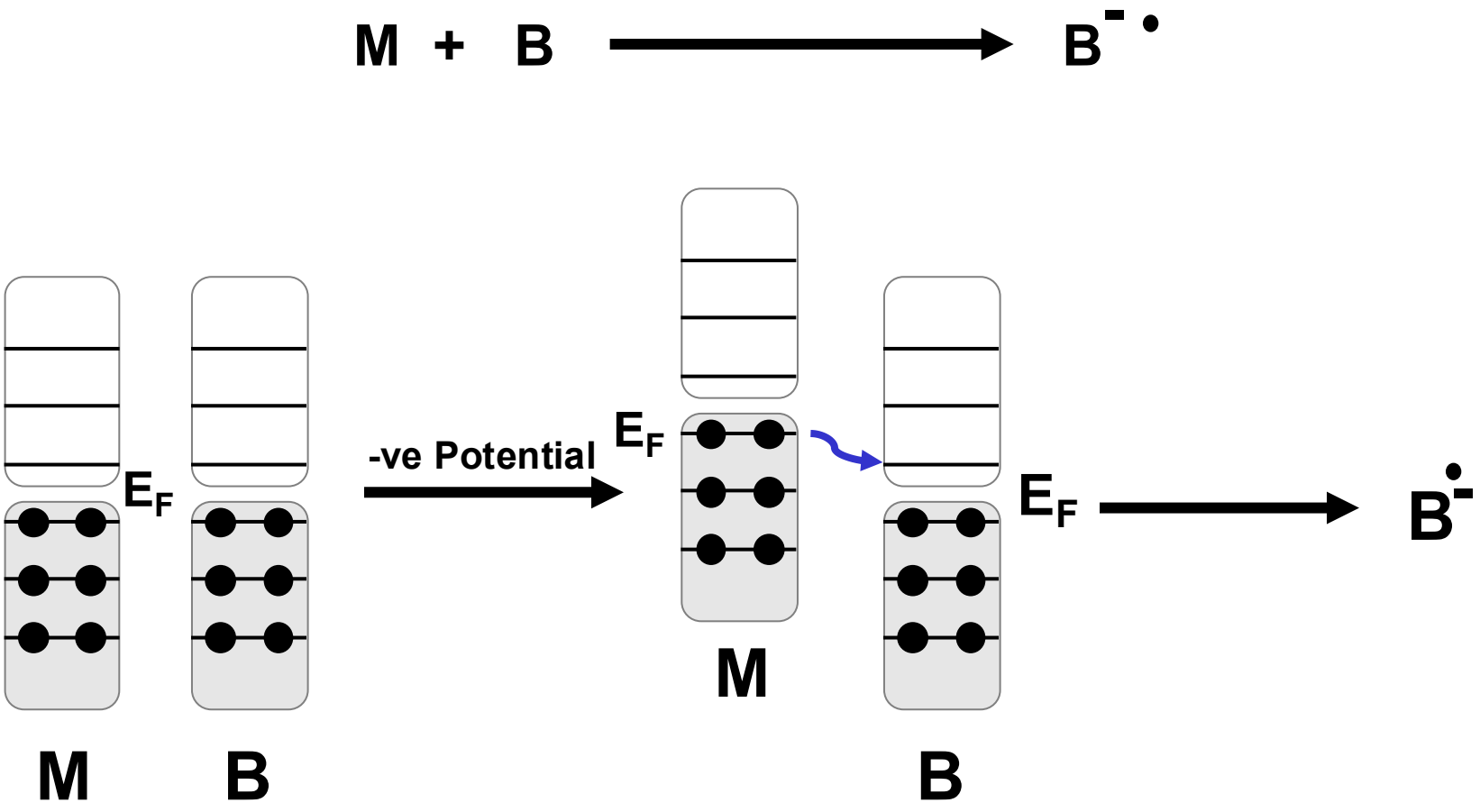


Fermi Levels Control Organic Chemistry ?

Electro Organic Chemistry

Electro Organic Chemistry

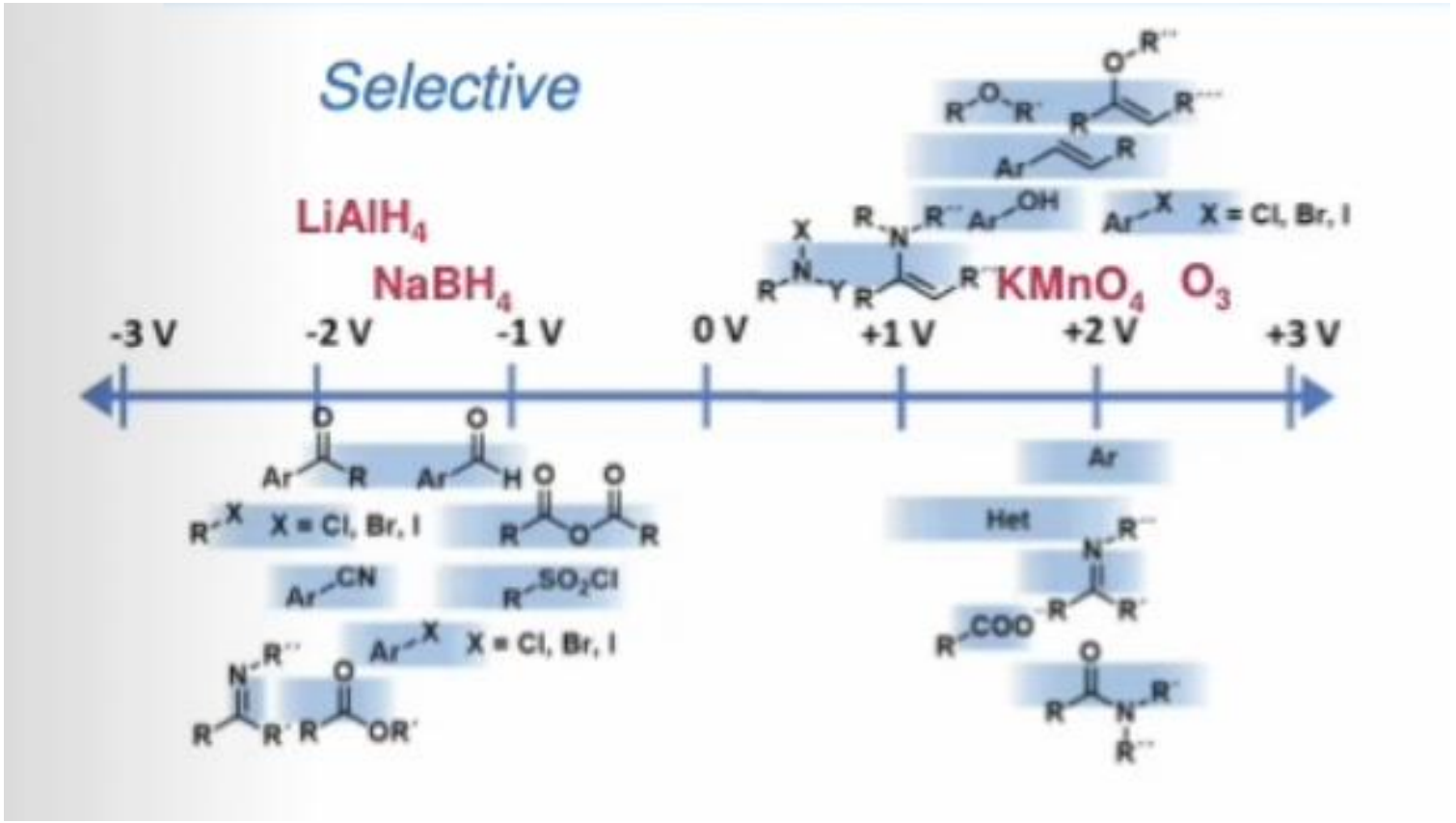


Fermi Levels Control Organic Chemistry ?

Electro Organic Synthesis

Access to Challenging Chemistries: 1eV = 23.1 kcal/mole

radicals, carbo cations and anions



If a high-field NMR can differentiate, Electro synthesis can also

Fermi Levels Control Organic Chemistry ?

Electro Organic Chemistry

Electro Organic Chemistry

- There is nothing like inherent Acid/Base or Nu/El or Ox/Red

Electro Organic Chemistry

Electro Organic Chemistry

- There is nothing like inherent Acid/Base or Nu/El or Ox/Red

- Infinite control of reactivity

Electro Organic Chemistry

Electro Organic Chemistry

- There is nothing like inherent Acid/Base or Nu/El or Ox/Red
- Infinite control of reactivity
- One electron transfer: Radical: Can react with itself

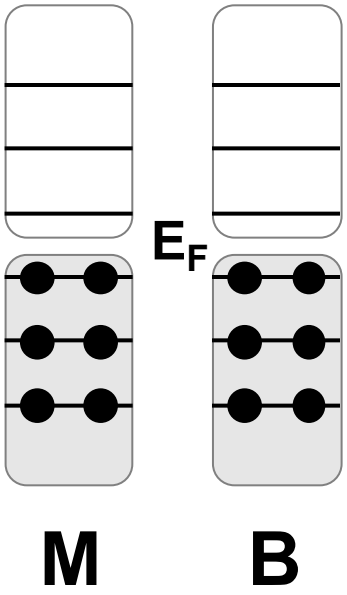
Electro Organic Chemistry

Electro Organic Chemistry

- There is nothing like inherent Acid/Base or Nu/El or Ox/Red
- Infinite control of reactivity
- One electron transfer: Radical: Can react with itself
- Two electron transfer: Ions: Can not react with itself

Electro Organic Chemistry

Electro Organic Chemistry



- Applied Potential (Infinite Reagents)
- Chemical Nature of Electrode
- Current Flow and Density
- Resistance (Distance between electrodes)
- Electrolyte
- Stirring
- Morphology of Electrodes
- Nature of Reacting Specie
- Surface Chemistry/Roughness of Electrode

A Golden Opportunity

Electro Organic Chemistry

Electro Organic Chemistry

A powerful synthetic tool

A simple electron : Thousands of chemical reagents

A simple electron : Precise control of reactivity/selectivity

A simple electron : Finer control of concentration

A simple electron : Reactivity can easily be reversed

A simple electron : Easy to start/stop (process safety)

A simple electron : Cheapest reagent

A simple electron : Green reagent

Electro Organic Chemistry

Electro Organic Chemistry

Electron: Safest Reagent

Concentration and Reactivity can be controlled externally

Language of Organic Chemistry is very different

Electro Organic Synthesis

Standard Electrode Potentials

All tabulated values of *standard electrode potentials* by convention are listed for a reaction written as a reduction, not as an oxidation

Overall cell reaction is sum of two half cell reactions

The cell potential is the difference between the reduction potentials:

$$E^{o}_{cell} = E^{o}_{cathode} - E^{o}_{anode}$$

$$\triangle G^{0} = -nFE^{0}$$

$$C = A.s$$

$$F = 96{,}486\ C/mol\ e^{-}$$

For Electro Organic Synthesis: E_{cell} will always be negative

Electro Organic Synthesis

The quantity of material that is oxidized or reduced at an electrode during an electrochemical reaction is determined by the stoichiometry of the reaction and the amount of charge that is transferred.

$Ag^+(aq) + e^- \rightarrow Ag(s)$, 1 mol of electrons reduces 1 mol of Ag^+ to Ag metal

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$, 1 mol of electrons reduces only 0.5 mol of Cu^{2+} to Cu metal

$$C = I\ (Amp)\ X\ t\ (Sec)$$

$$Mol\ of\ e^- = C / F = I.t / 96{,}486$$

The ampere is a measure of the rate of flow of electric charge, or electric current.

1C is 6.241×10^{18} charges

1F is one mole of charges = $(6.023 \times 10^{23}) / (6.241 \times 10^{18})$

Basic Electrochemistry

Bookshelves

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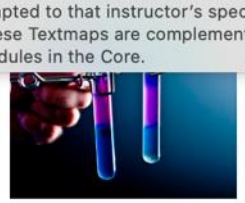
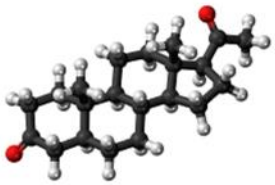
Introductory, Conceptual, and GOB Chemistry: Textbook Maps are an attempt to recreate that for existing textbooks to facilitate adoption. Faculty do not need to recreate the wheel to generate a LibreText for their class and can peruse the existing LibreTexts; then they can be adapted to that instructor's specific desires. These Textmaps are complemented by the Modules in the Core.

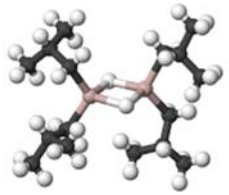


Introductory, Conceptual, and GOB Chemistry

General Chemistry

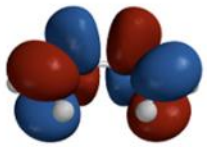


Organic Chemistry



Inorganic Chemistry

Analytical Chemistry



Physical & Theoretical Chemistry

Biological Chemistry

Environmental Chemistry

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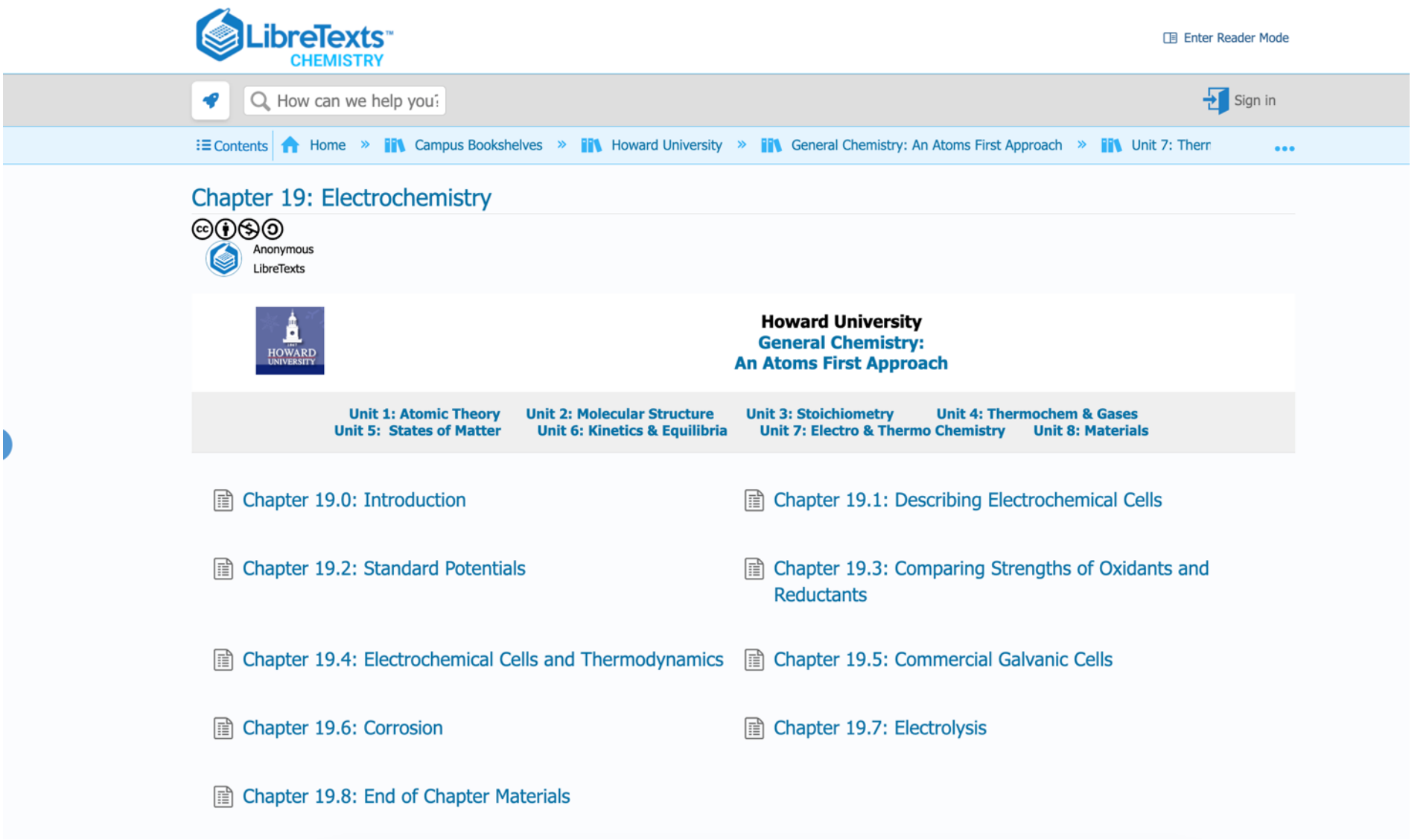
Basic Electrochemistry

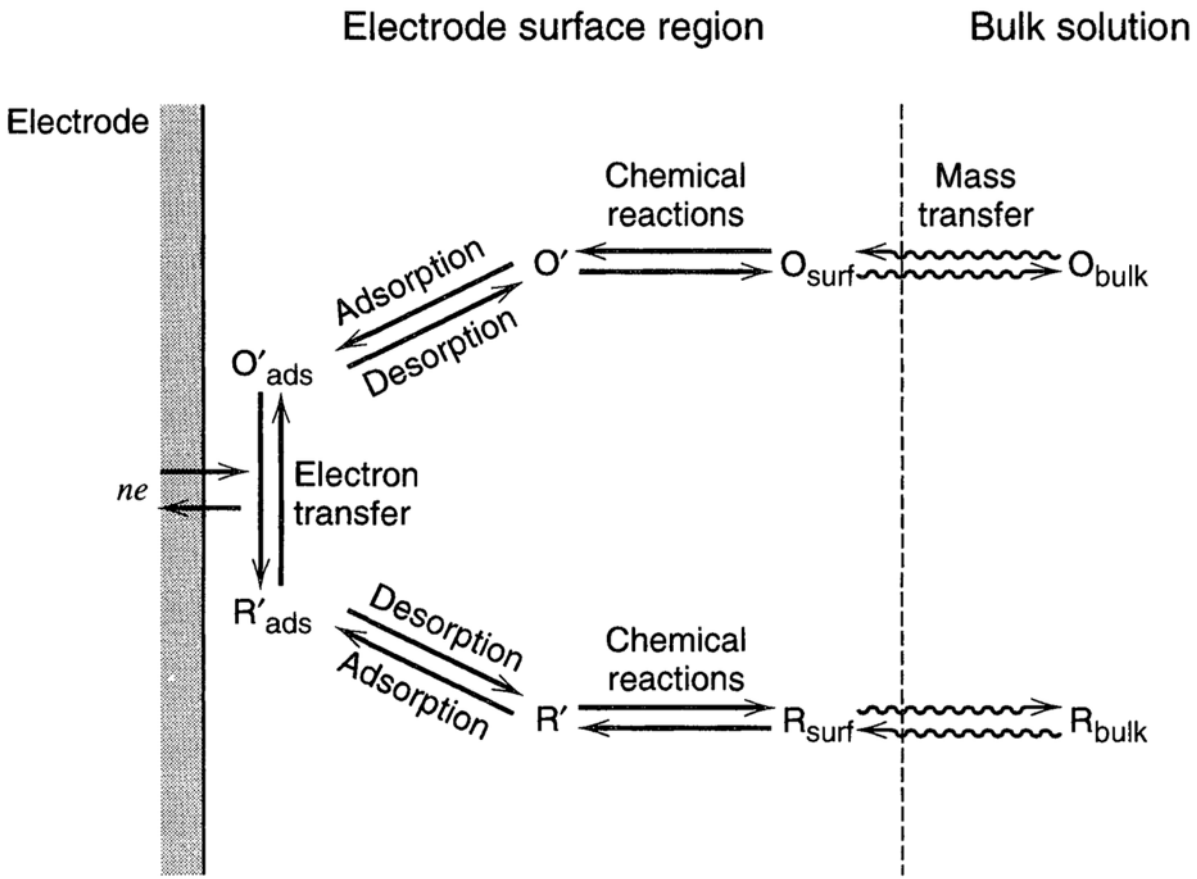


https://chem.libretexts.org/Courses/Howard_University/General_Chemistry%3A_An_Atoms_First_Approach/Unit_7%3A_Thermodynamics_and_Electrochemistry/Chapter_19%3A_Electrochemistry

Electro Organic Synthesis

Electrode Reaction Rate and Current

Direct Electrochemical Reaction

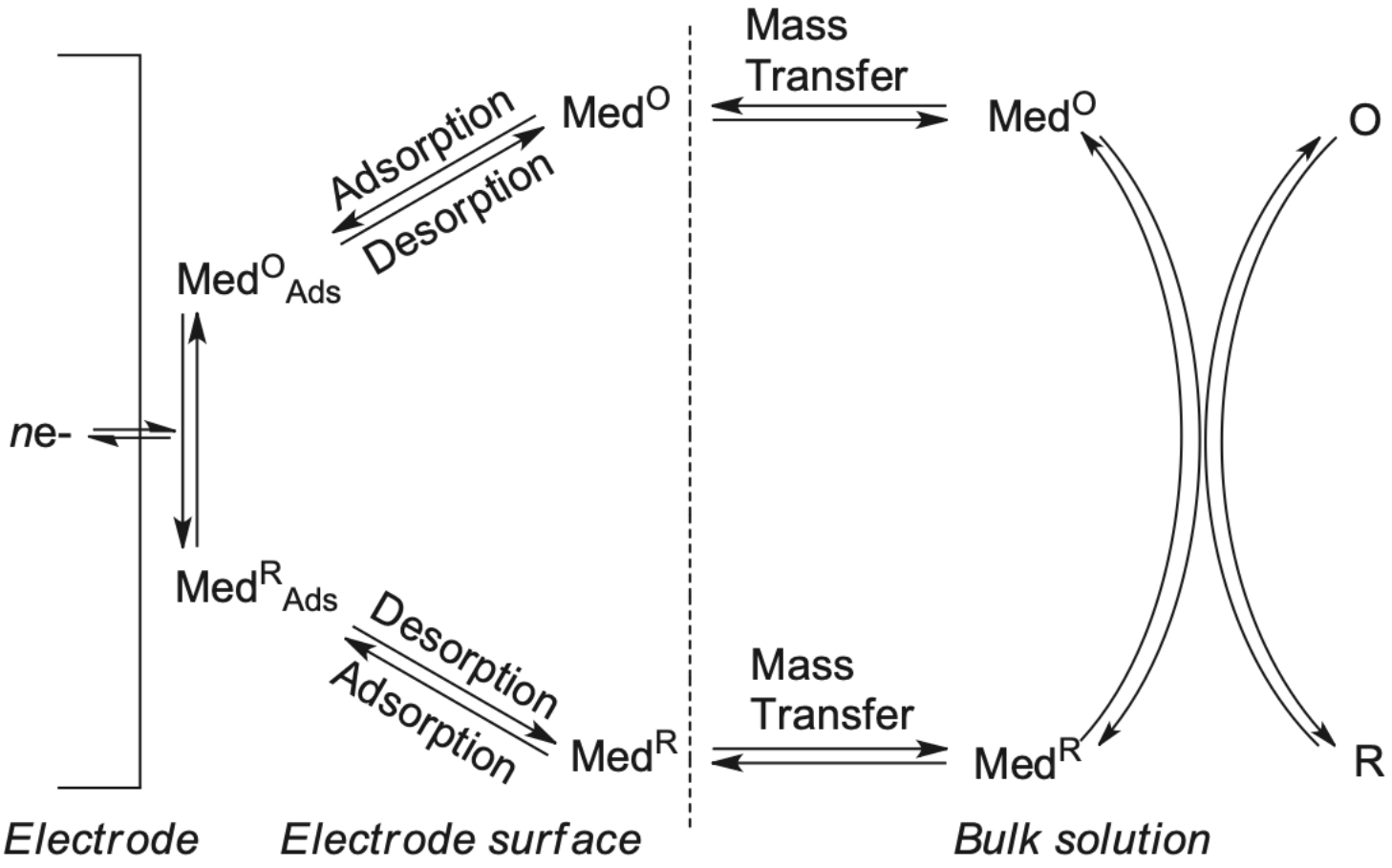


Bard and Faulkner, Electrochemical Methods, 2nd Ed.

Electro Organic Synthesis

Electrode Reaction Rate and Current

Indirect Electrochemical Reaction

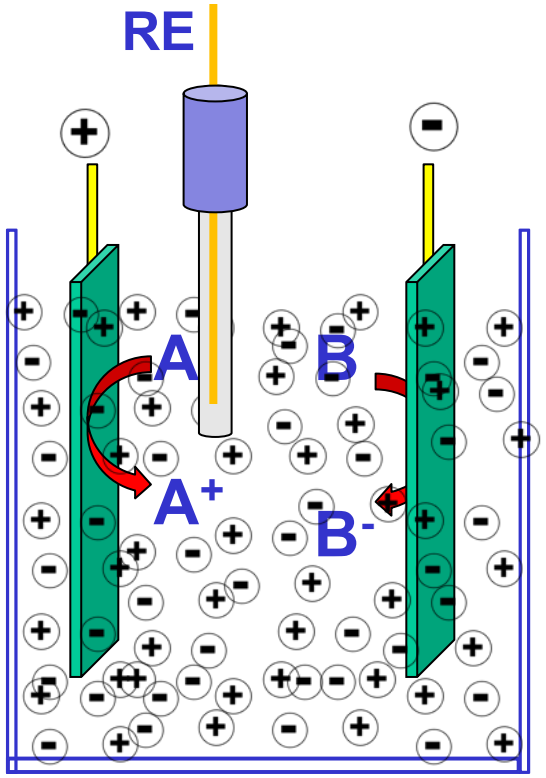


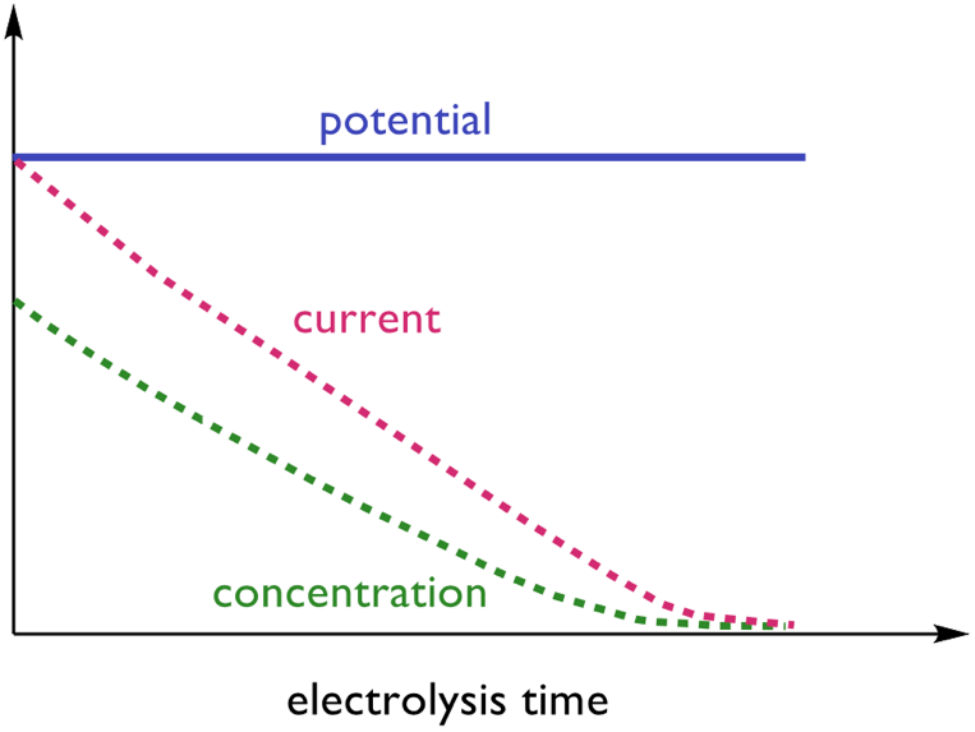
Bard and Faulkner, Electrochemical Methods, 2nd Ed.

Electro Organic Synthesis

Constant Potential

Cell Potential is kept constant



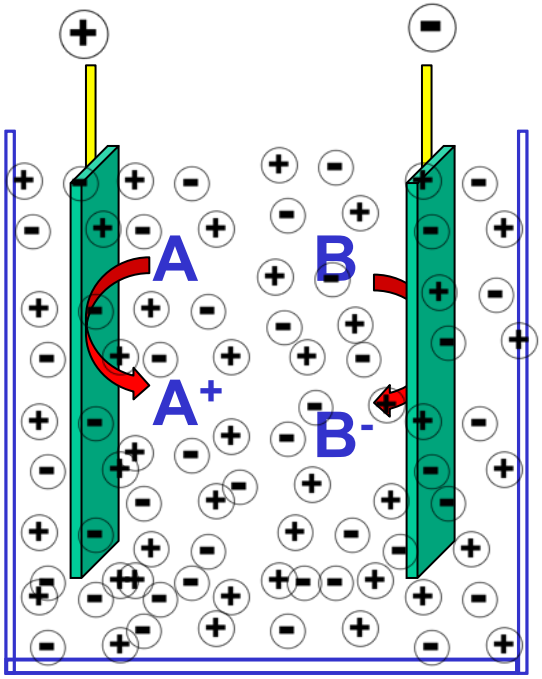


Potentiostat & Ref Electrode

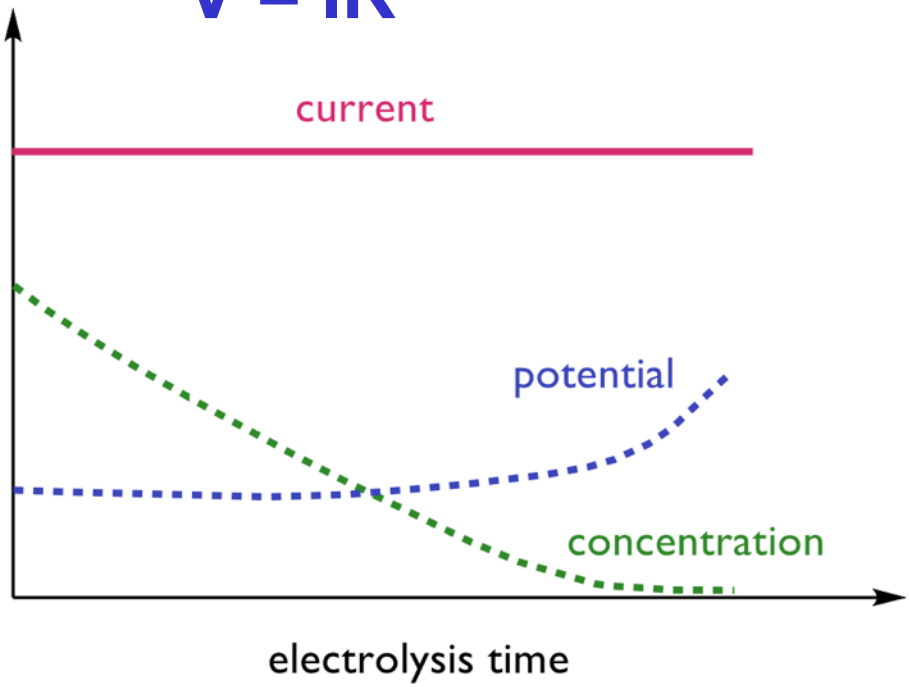
Electro Organic Synthesis

Constant Current

Current is kept constant



$$V = IR$$



Time (s) = Q (C) / A (Amp)

Simplest and Scalable

Electro Organic Lab Tools

Requirements:

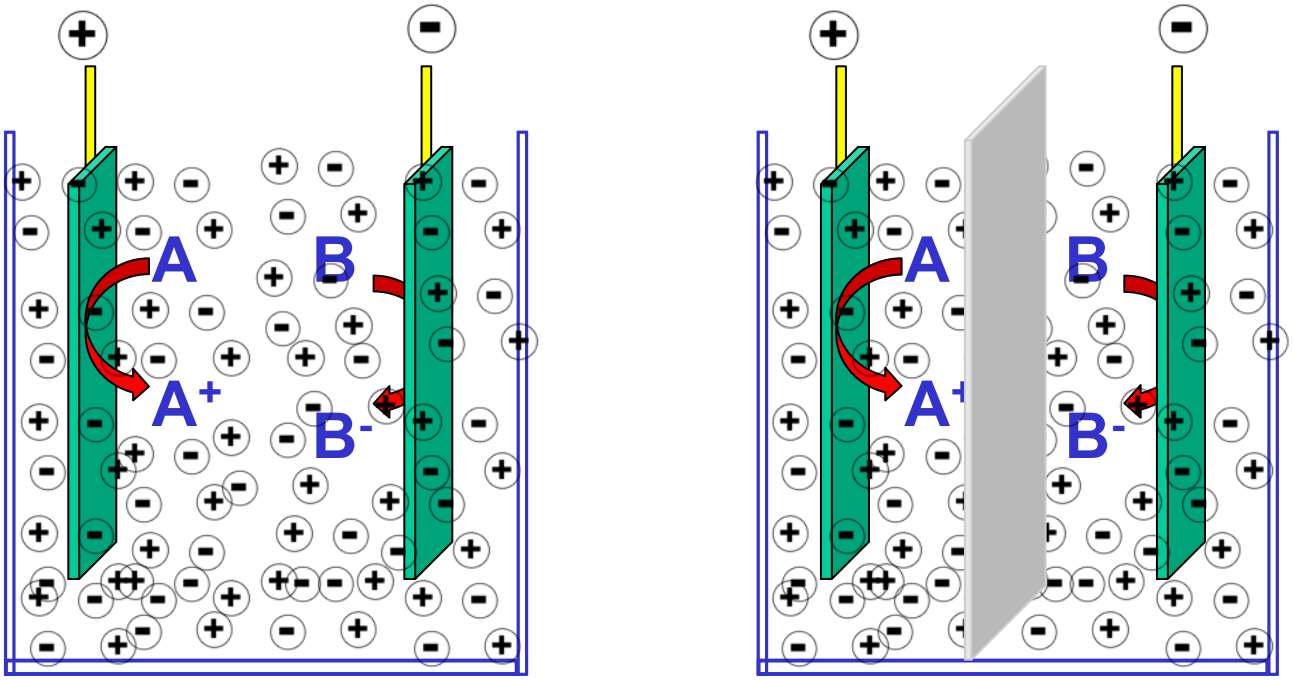
- Electrodes: Anode, Cathode and/or Reference Electrode
- Electrodes Gap and Area
- Reagents (Mediators, Catalysts etc)
- Solvent
- Electrolyte
- Stirring
- Power Supply: Simple current source (battery) or Potentiostat
- Electrochemical Cells

Electrochemical reaction can happen with

Electrode, Reagent, Solvent or Electrolyte

Electro Organic Lab Tools

Electrochemical Cells



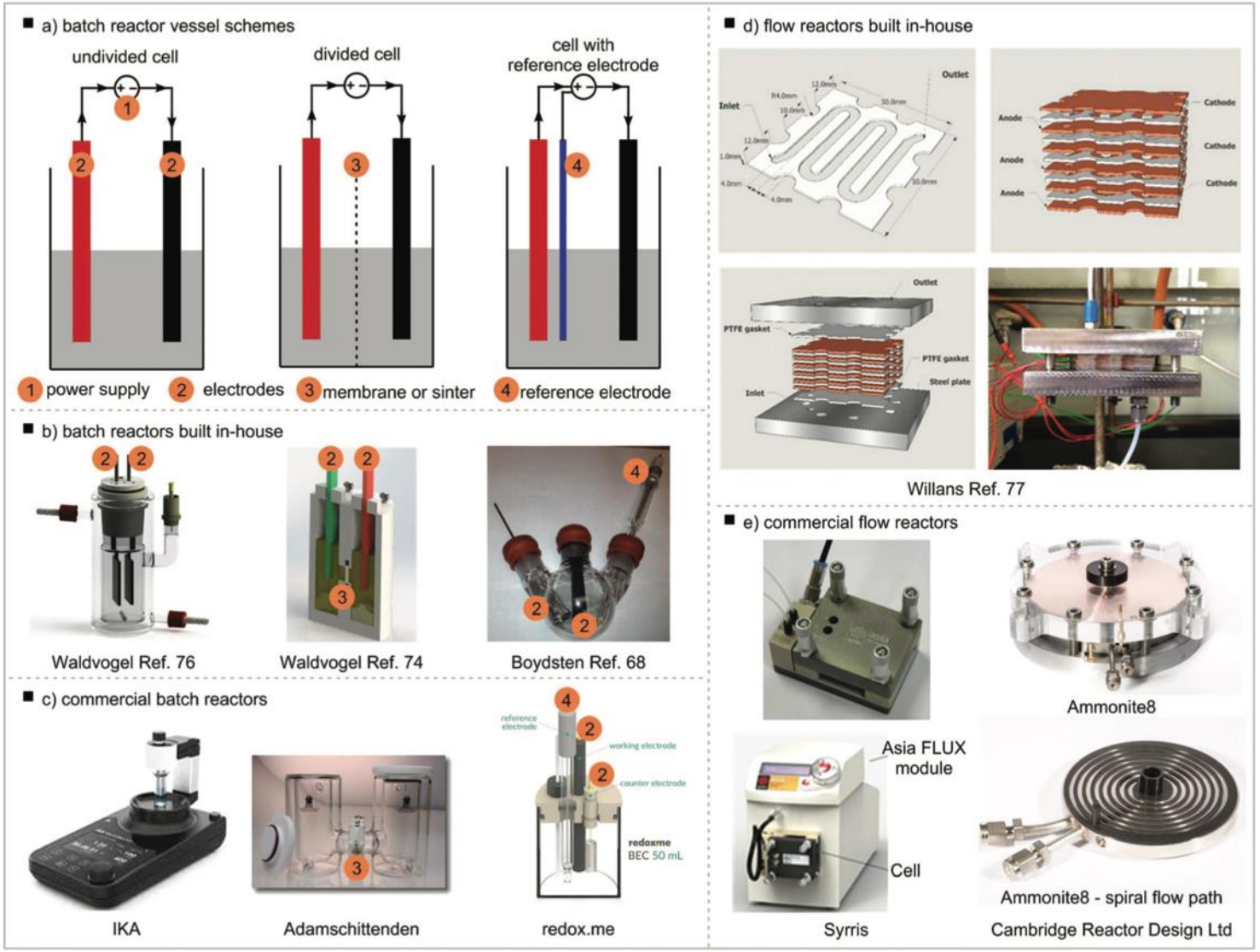
Divided vs Undivided Cells

Surface Area of Electrodes

Separation of Electrodes (Not too Close)

Electro Organic Lab Tools

Electrochemical Cells



Green Chem, 2020, 22, 3358-75

Continuous Flow Chemistry Lab

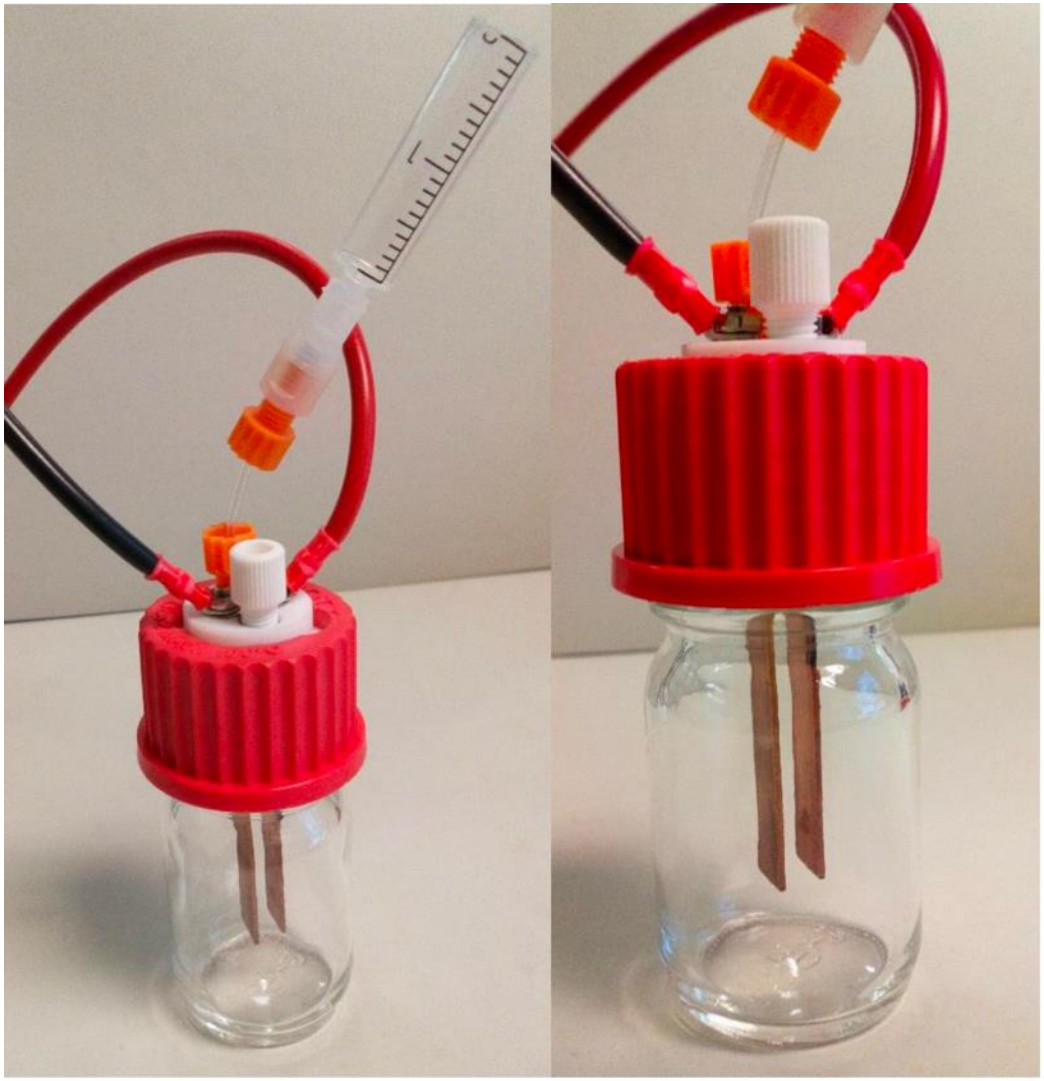
Electro Organic Lab Tools

Electrochemical Cells

Continuous Flow Chemistry Lab

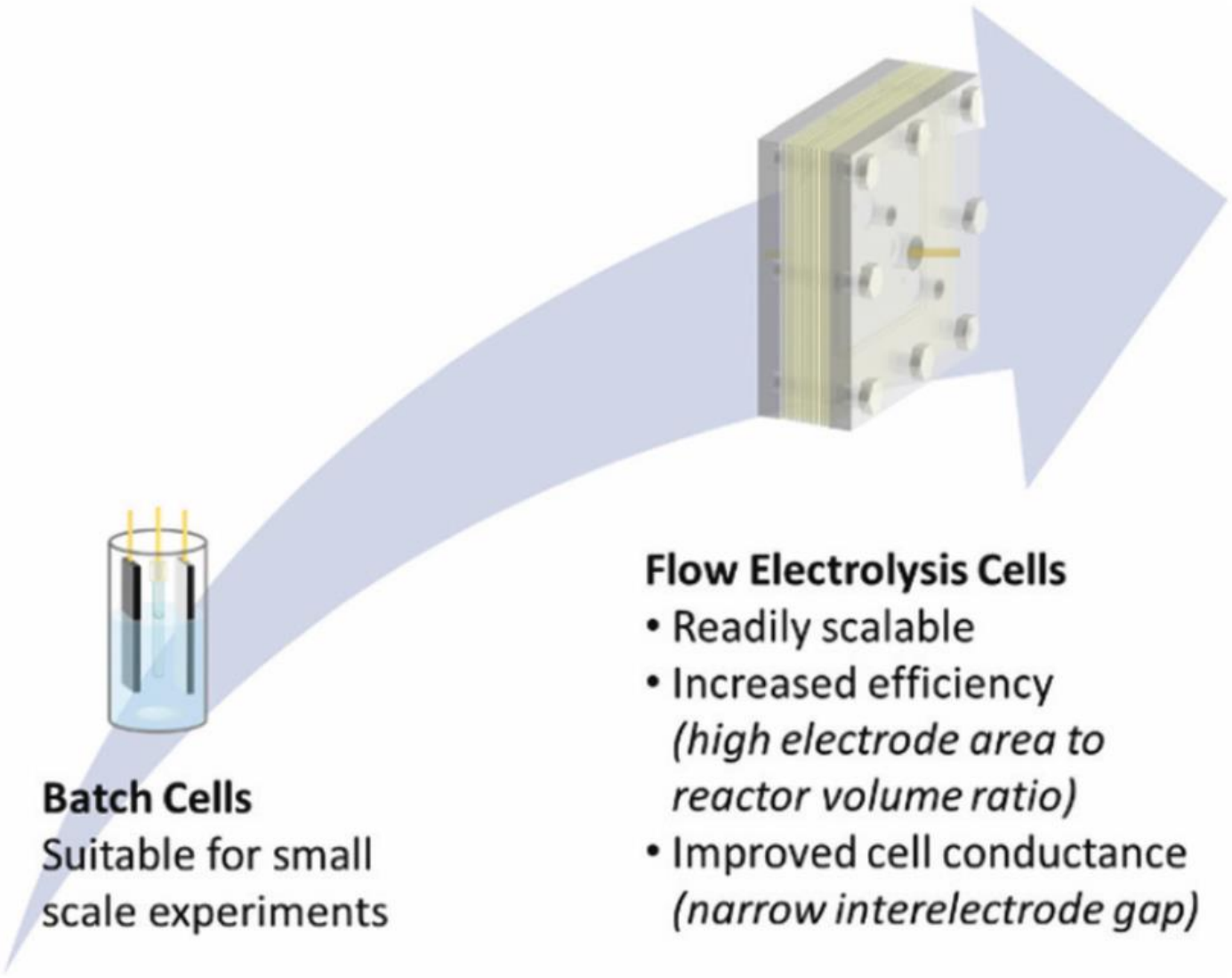
Electro Organic Lab Tools

Electrochemical Cells



Org. Process Res. Dev. 2020, 24, 6, 1084–1089

PI Process Intensification



Batch Cells
Suitable for small scale experiments

Flow Electrolysis Cells
- Readily scalable
- Increased efficiency *(high electrode area to reactor volume ratio)*
- Improved cell conductance *(narrow interelectrode gap)*

David Cantillo, Chem. Commun., 2022, 58, 619–628

Production Electro Flow Tools

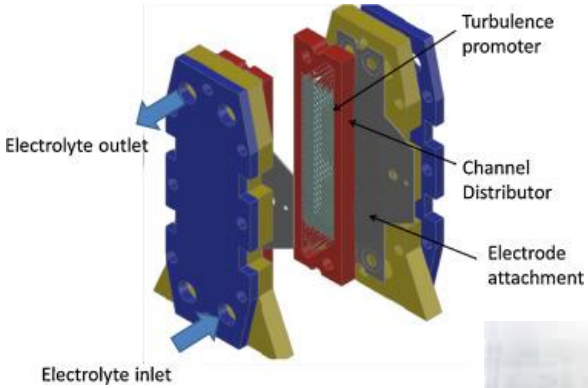
Micro Flow Cell

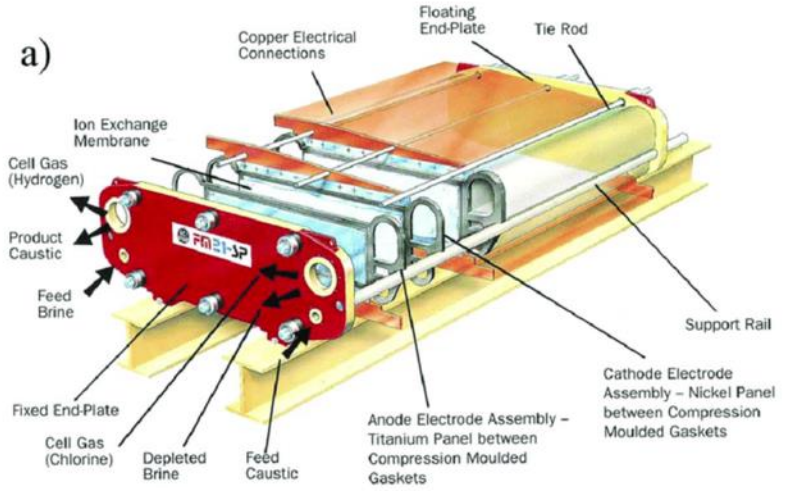
Electro MP Cell Electrode

Electro Syn Cell

Electro Prod Cell

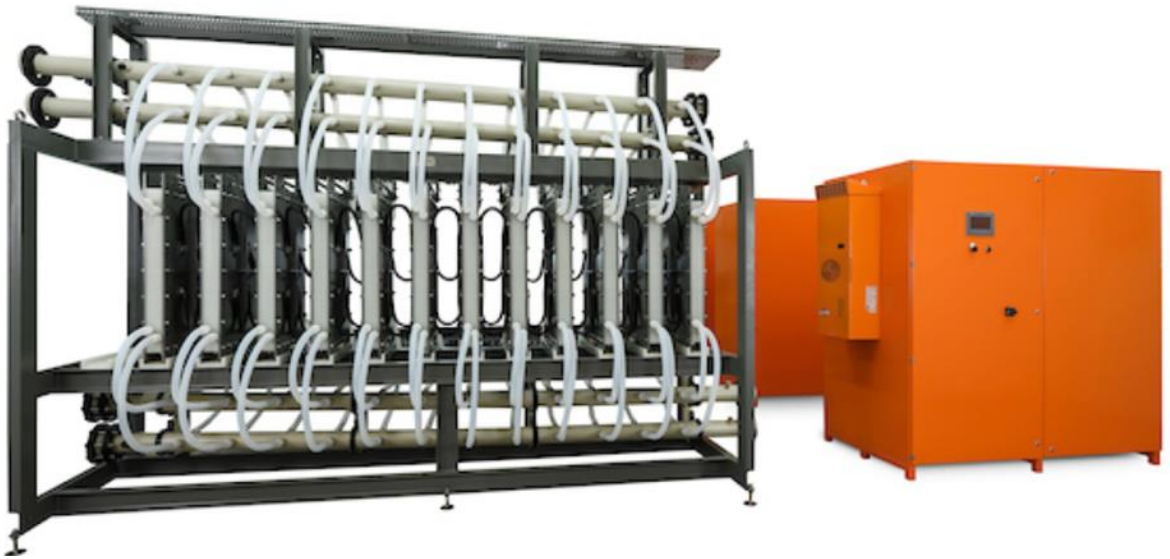
http://elxtechnologies.com/electro-cell-technologies.html





filter-press FM01-LC Flow Reactors (ICI)

Production Electro Flow Tools



C-Tech Innovation

India: Electro Production Facility

Axplora

India: Electro Production Facility

Axplora

Continuous Flow Chemistry Lab

Electro Organic Lab Tools

Electrodes

Anything which conducts: Metals, Semiconductors (polymers)

Continuous Flow Chemistry Lab

Electro Organic Lab Tools

Electrodes

Anything which conducts: Metals, Semiconductors (polymers)

Working and Counter Electrodes (Anode/Cathode)

Continuous Flow Chemistry Lab

Electro Organic Lab Tools

Electrodes

Anything which conducts: Metals, Semiconductors (polymers)

Working and Counter Electrodes (Anode/Cathode)

Reference Electrodes:

Stable potential, almost no current flow

Continuous Flow Chemistry Lab

Electro Organic Lab Tools

Electrodes

Anything which conducts: Metals, Semiconductors (polymers)

Working and Counter Electrodes (Anode/Cathode)

Reference Electrodes:

Stable potential, almost no current flow

Area: Counter Electrode > Working Electrode

Electro Organic Lab Tools

Electrodes

Anodes

Anode for Reduction

Mg Al Fe Ni Sn Pb Cu Hg Ag

Sacrificial anode (Dissolve when used as anode)

Anode for Oxidation

Au Pt Carbon-based

Non sacrificial anode

Cathodes

Cathode for Reduction

Mg Al Fe Sn Pb Hg Carbon-based

Good for reduction of organic compounds

Cathode for Oxidation

Fe Au Ni Pt

When HER Needed

Electro Organic Lab Tools

Electrodes

Carbon-based material:

- Graphite
- Glassy carbon,
- RVC (Reticulum Vitreous Carbon, porous glassy carbon
- Boron-doped diamond (BDD)

Electro Organic Lab Tools

Electrodes

Carbon-based material:

- Graphite
- Glassy carbon,
- RVC (Reticulum Vitreous Carbon, porous glassy carbon
- Boron-doped diamond (BDD)

Electro Organic Lab Tools

Electrodes

Carbon-based material:

- Graphite
- Glassy carbon,
- RVC (Reticulum Vitreous Carbon, porous glassy carbon
- Boron-doped diamond (BDD)

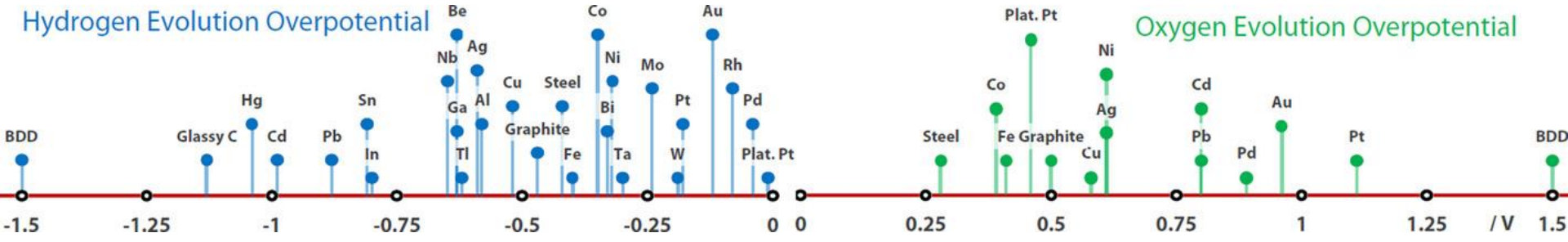
Cheaper Option
SS with Electroplating

Electro Organic Lab Tools

Electrodes

Electrode Material	H_2 Evolution η [a] /V H_2O	MeOH	O_2 Evolution η [c] /V H_2O	Conductivity [d] S/cm (10^4)
Ag	-0.59 [92], -0.46 [93]	-0.21 [92]	0.61 [94]	68.17
Al	-0.58 [93]			41.37
Au	-0.12 [92]	-0.20 [92]	0.96 [94]	48.76
Be	-0.63 [95]			33.11
Bi	-0.33 [92]	-0.32 [92]		0.93
Cd	-0.99 [93]		0.80 [94]	14.71
Co	-0.3-0.4 [96]		0.39 [94]	17.86
Cu	-0.46, [99] -0.57, [95] -0.60 [93]	-0.32 [99]	0.58 [94]	64.81
Fe	-0.40 [93]		0.41 [94]	11.67
Ga	-0.63 [b] [100]			7.35
Hg	-1.04 [93]			1.04
In	-0.80 [95]			12.50
Mo	-0.13, [92] -0.30 [95]	-0.28 [92]		20.62
Nb	-0.65 [95]			6.58

Electrode Material	H_2 Evolution η [a] /V H_2O	MeOH	O_2 Evolution η [c] /V H_2O	Conductivity [d] S/cm (10^4)
Ni	-0.32 [95]		0.61 [94]	16.23
Pb	-0.85, [95] -0.91 [93]		0.80 [94]	5.21
Pd	-0.01, [92] -0.09 [96]	-0.01 [92]	0.89 [94]	10.22
Pt	-0.27, [92] -0.09 [93]	-0.19 [92]	1.11 [94]	10.42
Plat. Pt	-0.01 [92]	-0.01 [92]	0.46 [94]	
Rh	-0.08 [93]			23.3
Sn	-0.81 [97]			8.70
Ta	-0.20, [92] -0.41 [95]	-0.36 [92]		8.20
Tl	-0.61, [92] -1.05 [95]	-0.44 [92]		6.67
W	-0.11, [92] -0.27 [93]	-0.32 [92]		20.75
S Steel	-0.42 [e] [101]		0.28 [e] [101]	1.40 [102]
Graphite	-0.47 [93]		0.50 [94]	0.0003, 0.4, [103] 2.6 [104]
BDD	-1.5 [f] [105]		1-2 [g] [105–107]	0.000001-0.002 [108]
GC (RVC)	-1.13 [h] [109]			0.02-0.10 [110]



Angew. Chem. Int. Ed., Eng., 2020, 59,18866-84

Continuous Flow Chemistry Lab

Electro Organic Lab Tools
Electrodes

Material		Inertness	Counter Reaction	Comments
Pt	Anode	✓	✓	Expensive
	Cathode	✓	▲	Competition through HER
Graphite	Anode	✓	▲	Porous material, cleaning routine important
	Cathode	✓	▲	
Glassy carbon	Anode	✓	▲	Similar to graphite but non-porous
	Cathode	✓	▲	
Reticulated vitreous carbon (RVC)	Anode	✓	▲	Similar to graphite but very high surface area
	Cathode	✓	▲	
SS) and Fe	Anode	✗	▲	Inexpensive, not suitable as anode, can get rusty
	Cathode	✓	▲	
Zn, Cu, Ni…	Anode	✗	✓	Suitable as sacrificial anode
	Cathode	✓	▲	

Electrode performance ranked in ✓: good, ▲: medium, ✗: bad.

Green Chem, 2020, 22, 3358-75

Continuous Flow Chemistry Lab

Electro Organic Lab Tools

Electrodes

Organic Electrochemistry

How to cite: *Angew. Chem. Int. Ed.* **2020**, *59*, 18866–18884
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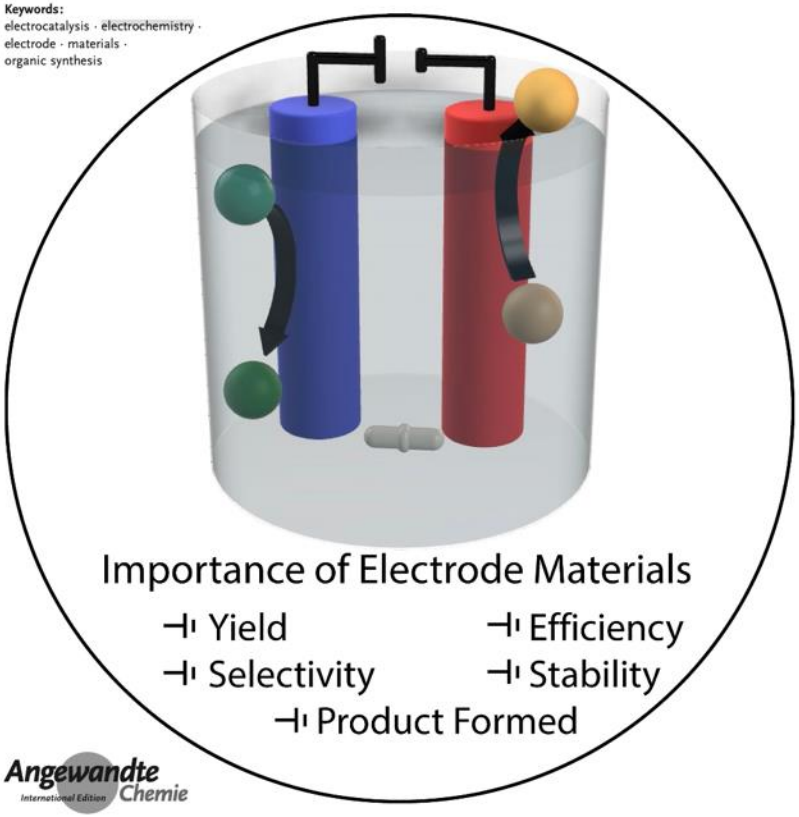
German Edition: doi.org/10.1002/ange.202005745

Electrode Materials in Modern Organic Electrochemistry

*David M. Heard and Alastair J. J. Lennox**

Keywords:
electrocatalysis · electrochemistry · electrode · materials · organic synthesis



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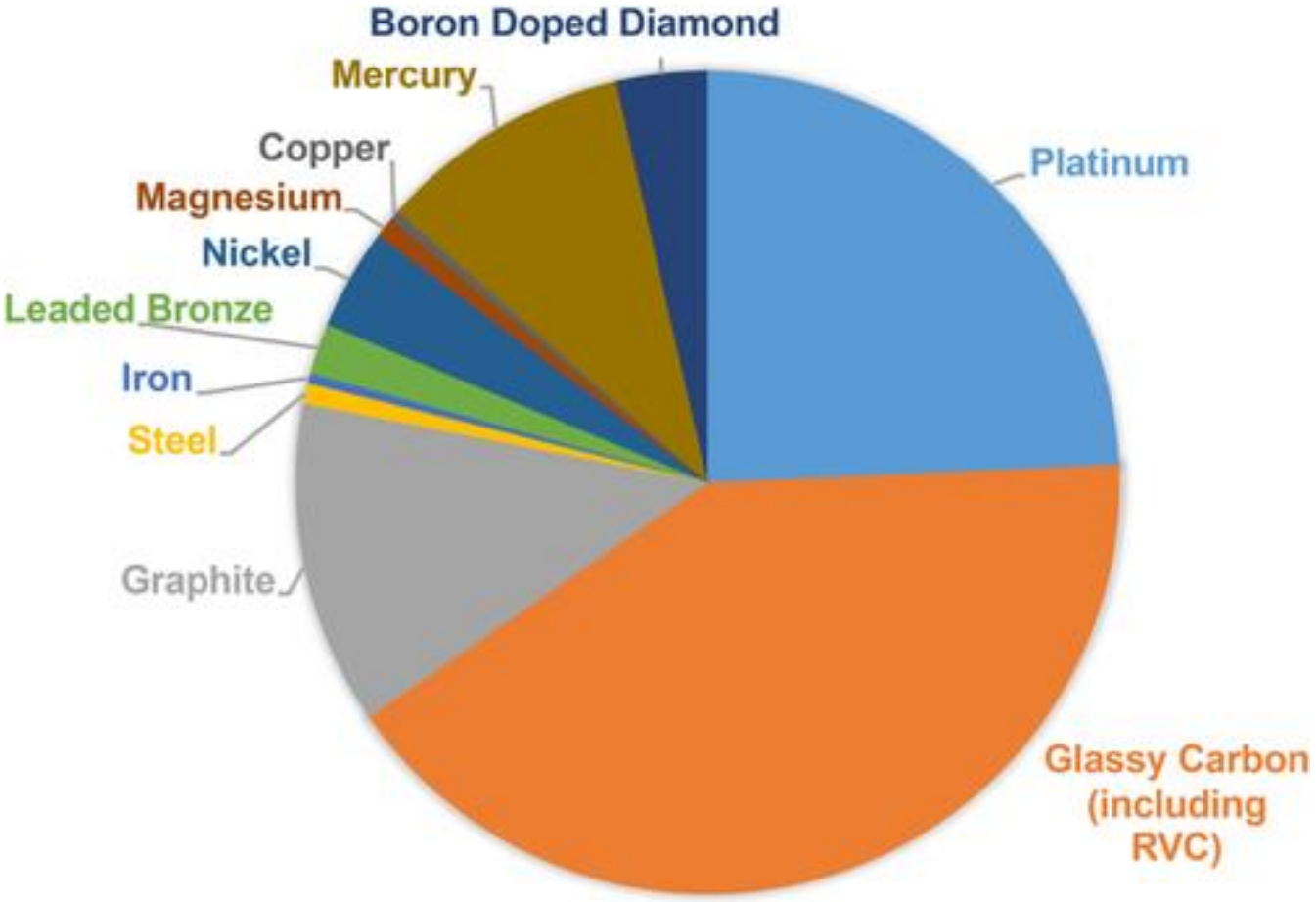
Continuous Flow Chemistry Lab

Electro Organic Lab Tools

Electrodes



Survey of 915 synthetic electrochemical protocols published between 2000–2017

Angew. Chem. Int. Ed., Eng., 2020, 59,18866-84

Continuous Flow Chemistry Lab

Electro Organic Lab Tools

Electrodes

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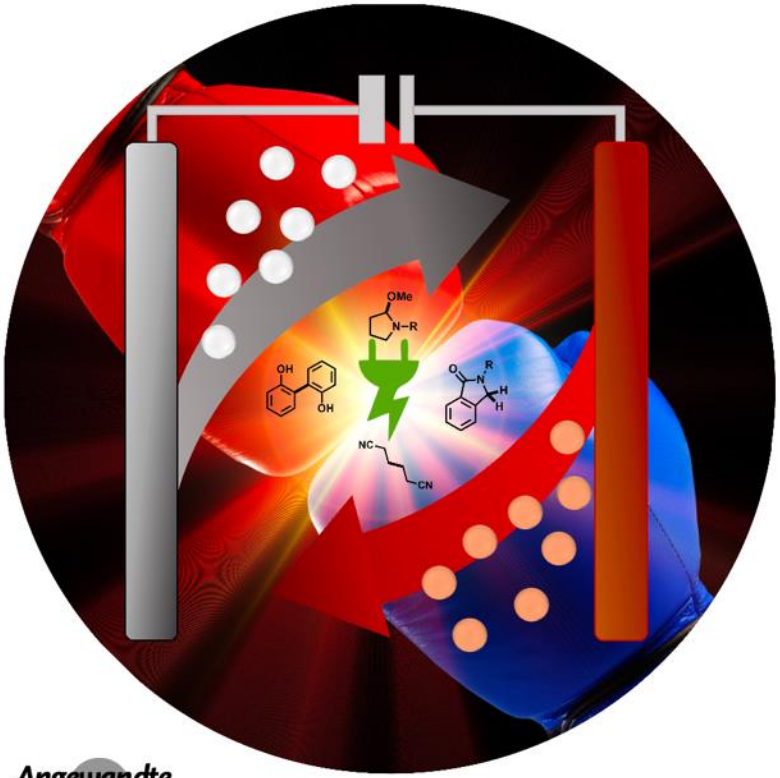
German Edition: doi.org/10.1002/ange.202204140

Electrochemistry

Counter Electrode Reactions—Important Stumbling Blocks on the Way to a Working Electro-organic Synthesis

*Martin Klein and Siegfried R. Waldvogel**



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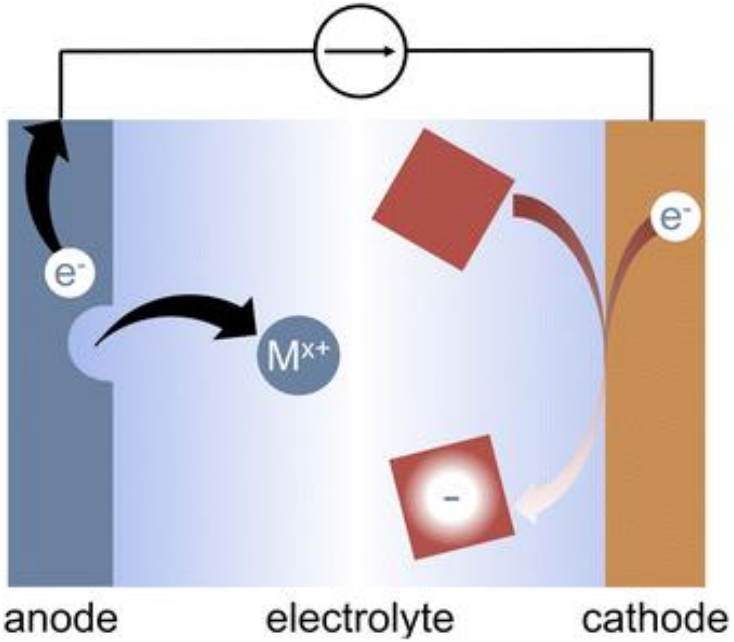
Continuous Flow Chemistry Lab

Electro Organic Lab Tools

Electrodes



DOI: 10.1039/D3SC06885D (Perspective) *Chem. Sci.*, 2024, **15**, 5814-5831

A guide to troubleshooting metal sacrificial anodes for organic electrosynthesis

Skyler D. Ware [a], **Wendy Zhang** [a], **Weiyang Guan** [b], **Song Lin** [b] **and Kimberly A. See** *[a]

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[b] *Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York 14853, USA*

Continuous Flow Chemistry Lab

Electro Organic Lab Tools

Electrolytes/Solvents

- Ionic salt
- Good solubility in organic solvents
- Inert during a reaction
- Concentration: 0.1-0.5 M

Cation: Li+, R4N+

Anion: BF4, PF6 , ClO4 , triflate, halide

IONIC LIQUID

ionic liquid		density (g/cm^3)	viscosity (mPa·s)	conductivity (mS/cm)	potential window (V vs Li^+/Li^c) E_{red}	E_{ox}
[emim][$AlCl_4$]	8	1.29	18	22.6	1.0	5.5
[emim][$H_{2.3}F_{3.3}$]	−9.0	1.14	5	10.0	1.5	5.3
[emim][BF_4]	11	1.24	43	13.0	1.0	5.5
[emim][CF_3CO_2]	−14	1.29[b]	35[b]	9.6[a]	1.0[d]	4.6[d]
[emim][CH_3SO_2]	39	1.25	160	2.7	1.3[d]	4.9[d]
[emim][CF_3SO_2]	−10	1.38	43	9.3	1.0	5.3
[emim][$(CF_3SO_2)_2N$]	−15	1.52[b]	28	8.4	1.0	5.7
[emim][$(C_2F_5SO_2)_2N$]	−1		61	3.4	0.9	5.8
[emim][$(CF_3SO_2)_3C$]	39		181	1.7	1.0	6.0

[a] 20 °C. [b] 22 °C. [c] GC (glassy carbon), 1 mA·cm^{-2}, 20 mV·s^{-2}. [d] Pt, 50 mV ·s^{-1}, emim = 1-ethyl-3-methydazolium.

Green Chem, 2020, 22, 3358-75

Continuous Flow Chemistry Lab

Electro Organic Lab Tools

Electrolytes/Solvents

Solvent	Electrolyte	Electrode	Cathodic limit (V)	Anodic limit (V)	Window (V)
H_2O	0.1 M KCl	C	−1.3	+1.1	2.4
	1 M KCl	Hg	−1.7	0	1.7
	TBA ClO_4	Hg	−2.0		
	$HClO_4$	Pt		+1.5	
MeCN	0.1 M TBA BF_4	Pt	−3.1	+3.2	6.3
	$LiClO_4$	Pt	−3.5	+2.4	5.8
DMF	0.1 M TBA ClO_4	Pt	−2.2	+1.7	3.9
Pyridine	$LiClO_4$	Hg	−1.7		
	$LiClO_4$	C		+1.4	
DMSO	0.01 M TBA PF_6	Pt	−1.0	+1.0	2
THF	$LiClO_4$	Pt	−3.6	+1.8	5.4
DCM	0.1 M TBA ClO_4	Au	−1.5	+2.0	3.5
	TBA ClO_4	Pt	−1.7	+1.8	3.5
HFIP	0.1 M TBA ClO_4	Pt	+0.8	+2.9	2.1
	0.1 M TBA ClO_4	C	−1.6	+3.1	4.7
	0.1 M RbF	C	−1.1	+3.4	4.5
MeOH	$LiClO_4$	Pt	−1.0	+1.3	2.3
MeCOOH	TEA ClO_4	Hg	−1.7		
	NaOAc	Pt		+2.0	

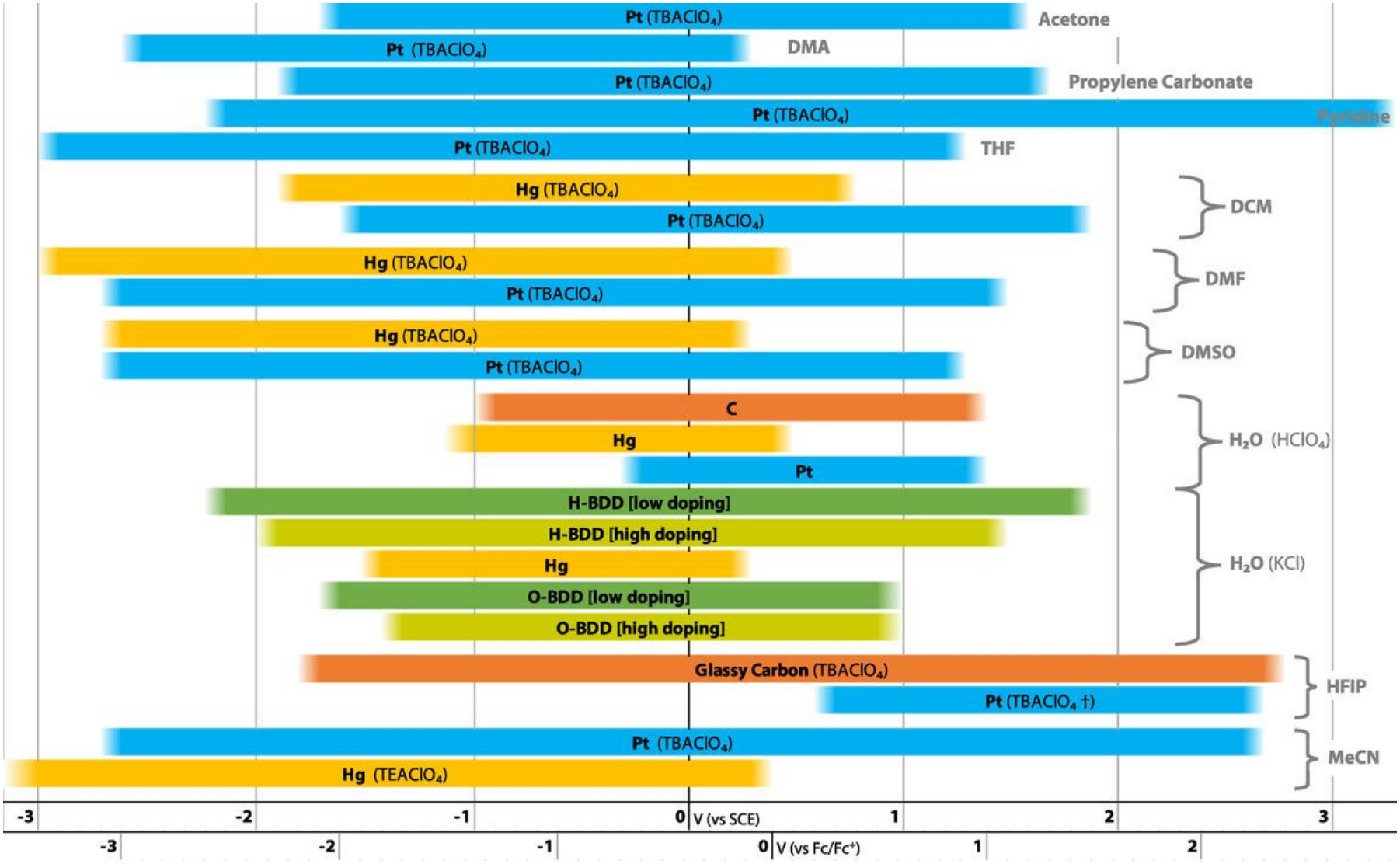
Values referenced to SCE (saturated calomel electrode), taken from the following ref. 110–113.

HFIP/DIPEA

(Chem. Rev. 2022, 122, 15, 12544–12747)

Green Chem, 2020, 22, 3358-75

Electro Organic Lab Tools



Solvent windows for various electrode material and electrolyte combinations

84

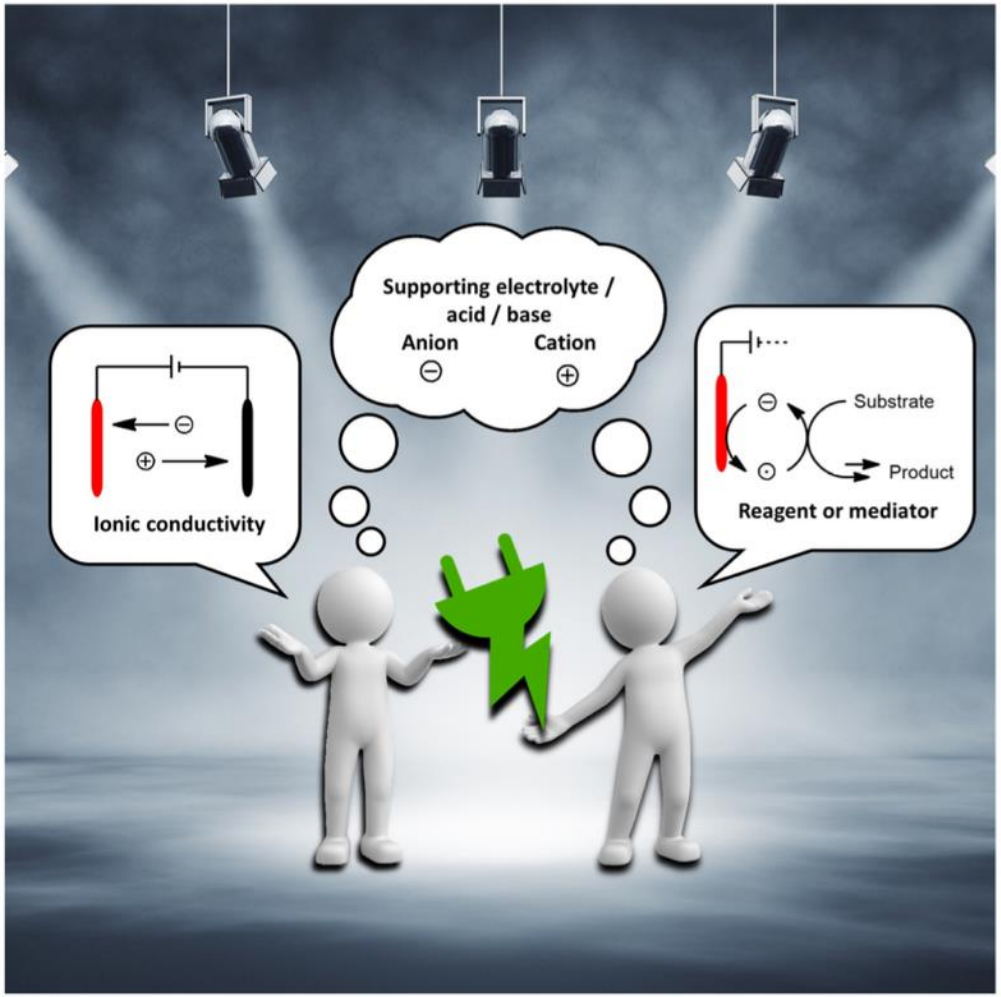
Angew. Chem. Int. Ed., Eng., 2020, 59,18866-84

Continuous Flow Chemistry Lab

Electro Organic Synthesis

Dual Roles of Supporting Electrolytes in Organic Electrosynthesis

Lilla G. Gombos[+],[a] Joachim Nikl[+],[a] and Siegfried R. Waldvogel*[a, b, c]



ChemElectroChem

Review
doi.org/10.1002/celc.202300730

Electro Organic Lab Tools

Potentiostat and Power supplies

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Electro Organic Lab Tools

Requirements:

- Electrodes: Anode, Cathode and/or Reference Electrode
- Electrodes Gap and Area
- Reagents (Mediators, Catalysts etc)
- Solvent
- Electrolyte
- Stirring
- Power Supply: Simple current source (battery) or Potentiostat
- Electrochemical Cells

Electrochemical reaction can happen with

Electrode, Reagent, Solvent or Electrolyte

Electro Organic Lab Tools

Practical Tips

Continuous Flow Chemistry Lab

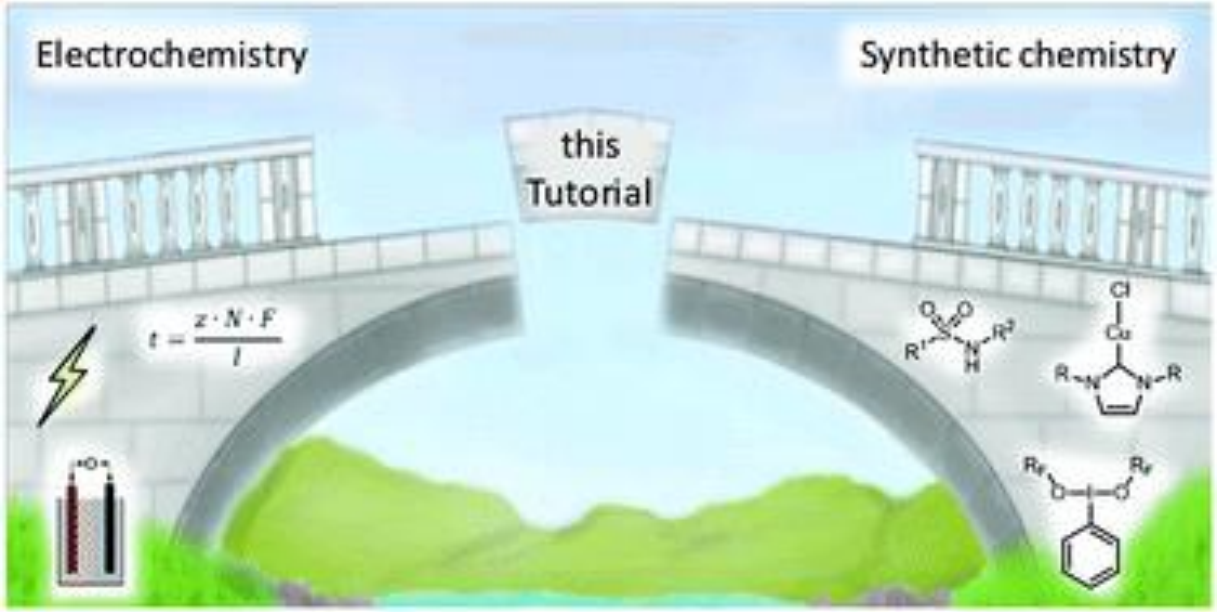
Issue 11, 2020

From the journal:
Green Chemistry

Making electrochemistry easily accessible to the synthetic chemist

Check for updates

Christiane Schotten,*[a] Thomas P. Nicholls,[a] Richard A. Bourne,[b] Nikil Kapur,[c] Bao N. Nguyen[a] and Charlotte E. Willans*[a]



Green Chem, 2020, 22, 3358-75

Electro Organic Lab Tools

Practical Tips

The initial reaction setup should be kept as simple as possible.

The following conditions are usually used as a starting point:

Anode: Graphite or Pt

Cathode: Stainless steel or Pt

Substrate: 20 to 50 mM

Electrolyte: 100 mM ($TBABF_4$ for Organic, KF/KCl salts for Aqueous);

Constant Current Mode: 20-50 mA, 1–2 F mol−1

Monitoring of the reaction by TLC, GC, LCMS etc. over time

Electro Organic Lab Tools

	Reaction mode	Current	Potential	Resistance	Reaction rate	Selectivity
Current ↑	Galvanostatic	↑	↑	Constant	↑	Potentially compromised due to increased potential Ohmic heating possible
Potential ↑	Potentiostatic	↑	↑	Constant	↑	Potentially compromised due to increased potential
Surface area ↑	Galvanostatic Potentiostatic	Constant ↑	↓ Constant	↓	Constant ↑	Constant or better Ohmic heating possible
Surface area ↓	Galvanostatic Potentiostatic	Constant ↓	↑ Constant	↑	Constant ↓	Potentially compromised due to increased potential Constant or better
Electrode gap ↑	Galvanostatic Potentiostatic	Constant ↓	↑ Constant	↑	Constant ↓	Potentially compromised due to increased potential Constant or better
Electrode gap ↓	Galvanostatic Potentiostatic	Constant ↑	↓ Constant	↓	Constant ↑	Constant or better Ohmic heating possible
Electrolyte concentration ↑	Galvanostatic Potentiostatic	Constant ↑	↓ Constant	↓	Constant ↑	Constant or better Ohmic heating possible
Electrolyte concentration ↓	Galvanostatic Potentiostatic	Constant ↓	↑ Constant	↑	Constant ↓	Constant or better Potentially compromised due to increased current density
Stirring ↑	Galvanostatic Potentiostatic	Constant ↑	↓ Constant	↓	Constant ↑	Constant or better Ohmic heating possible

Green Chem, 2020, 22, 3358-75

Electro Organic Lab Tools

Optimization

- Max Yield
- High Selectivity
- Max Current Density
- High Faradaic Efficiency (paired is best)
- Cost of Electrode Material
- Cost of Solvent
- Cost of Electrolyte
- Undivided Cell

Electro Organic Synthesis

- Inexpensive
- Atom Economic
- Selective
- Low Waste
- Access to Unusual and New Chemistry

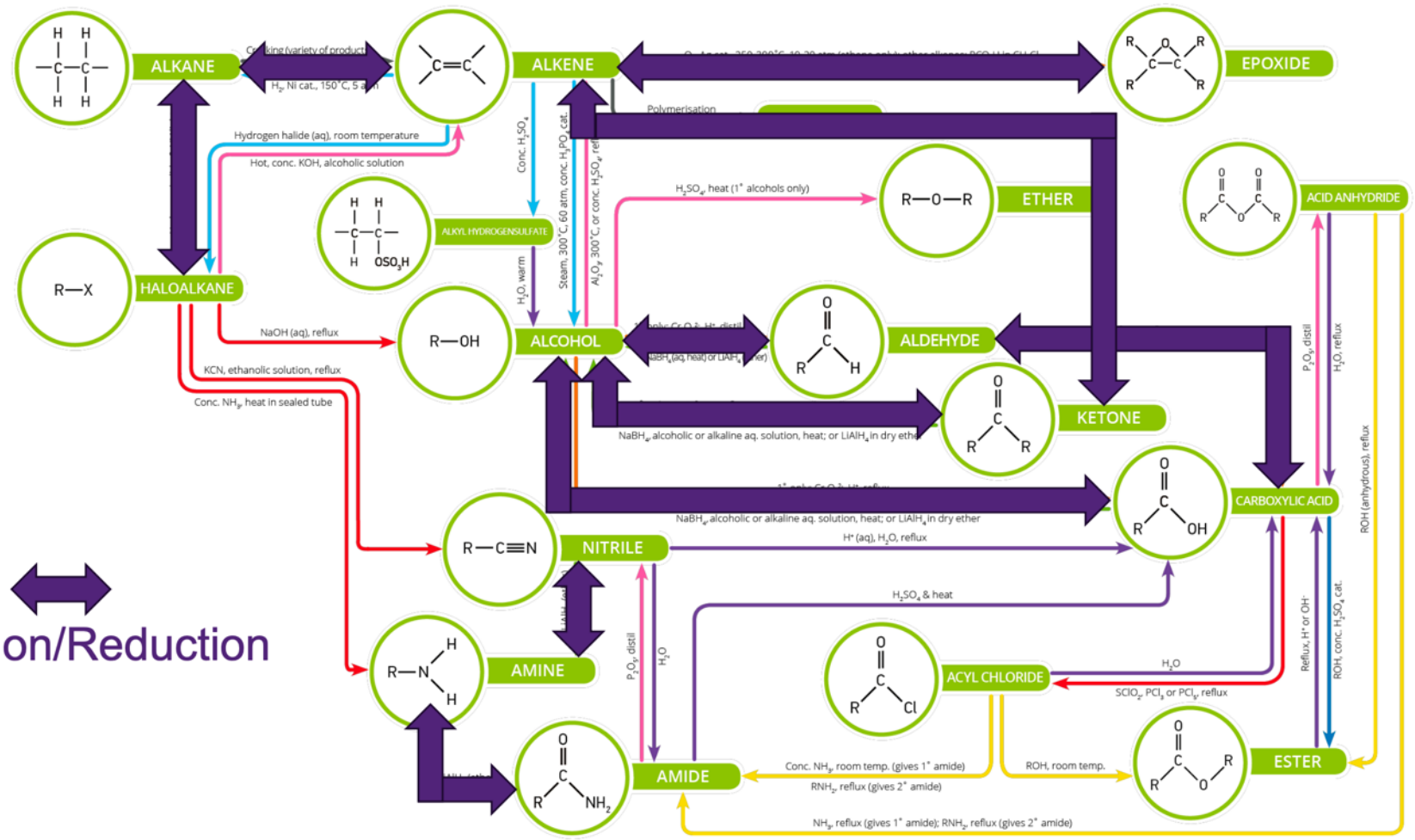
Electro Organic Lab Tools

Chemical	vs	Electrochemical
Substrate		Substrate
Reagent		Electricity
Solvent		Solvent
Catalyst		(Mediator)
		Electrodes
		Electrolyte
		Constant I or V
Flask		(Un)Divided Cell

The number of experimental parameters that may be manipulated in electrosynthesis is large

Electro Organic Chemistry

Organic Reactions Map



Slide: Prof. Cantillo, Univ of Queensland, Australia

Electro Organic Chemistry

Chemical vs Electrochemical

Oxidizing Agent — **Anode**

Reducing Agent — **Cathode**

$$3\ \text{Ar-CH}_2\text{OH} + 2\ \text{Cr}_2\text{O}_7^{2-} + 16\ \text{H}^+ \rightarrow 3\ \text{Ar-COOH} + 4\ \text{Cr}^{3+} + 11\ \text{H}_2\text{O}$$

$$\text{Ar-CH}_2\text{OH} + \text{H}_2\text{O} \rightarrow \text{Ar-COOH} + 4\ \text{e}^- + 4\ \text{H}^+$$

$$\text{Ar-NO}_2 + 3\ \text{Sn} + 7\ \text{H}^+ \rightarrow \text{Ar-NH}_3^+ + 3\ \text{Sn}^{2+} + 2\ \text{H}_2\text{O}$$

$$\text{Ar-NO}_2 + 6\ \text{e}^- + 7\ \text{H}^+ \rightarrow \text{Ar-NH}_3^+ + 2\ \text{H}_2\text{O}$$

Continuous Flow Chemistry Lab

Electro Organic Chemistry

Organic electrochemical conversions

Additions:

$R\text{-}CH{=}CH\text{-}R + 2Nu^- \rightarrow R\text{-}CHNu\text{-}CHNu\text{-}R + 2e^-$

$R\text{-}CH{=}CH\text{-}R + 2e^- + 2H^+ \rightarrow R\text{-}CH_2\text{-}CH_2\text{-}R$

Substitutions:

$R\text{-}CH_3 + Nu^- \rightarrow R\text{-}CH_2Nu + 2e^- + H^+$

$R\text{-}Cl + CO_2 + 2e^- \rightarrow R\text{-}COO^- + Cl^-$

Eliminations:

$R\text{-}CH_2\text{-}CH_2\text{-}R \rightarrow R\text{-}CH{=}CH\text{-}R + 2e^- + 2H^+$

$R\text{-}CHNu\text{-}CHNu\text{-}R + 2e^- \rightarrow R\text{-}CH{=}CH\text{-}R + 2Nu^-$

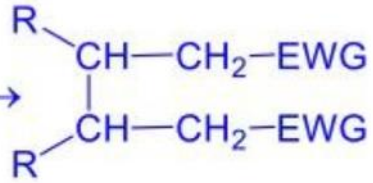
Cleavages:

$RS\text{-}SR \rightarrow 2RS^+ + 2e^- \rightarrow$ further reaction of RS^+

$RS\text{-}SR + 2e^- \rightarrow 2RS^-$

Couplings:

$2R\text{-}H \rightarrow R\text{-}R + 2e^- + 2H^+$

$2R\text{-}CH{=}CH\text{-}EWG + 2e^- + 2H^+ \rightarrow$ 

(Hydrodimerization)

Slide: Prof. Ole Hammerich, Univ of Copenhagen

Electro Organic Chemistry

The electrode potential - the driving force

- The Nernst equation
- The standard potential, E^o and the formal potential, $E^{o'}$

The heterogenous electron transfer rate constants, k_s^{red} and k_s^{ox}

$$O + ne \underset{k_s^{ox}}{\overset{k_s^{red}}{\rightleftharpoons}} R$$

$$E = E^o + \frac{RT}{nF}\ln\frac{(O)}{(R)} = E^o + \frac{RT}{nF}\ln\frac{f_O[O]}{f_R[R]}$$

$$E = E^{o'} + \frac{RT}{nF}\ln\frac{[O]}{[R]}$$

$$E^{o'} = E^o + \frac{RT}{nF}\ln\frac{f_O}{f_R}$$

n is the number of electrons (for organic compounds, typically, *n* = 1)
R is the gas constant
T is the absolute temperature
F is the Faraday constant
Parentheses, (), are used for activities and brackets, [], for concentrations
f_O and f_R are the activity coefficients of O and R, respectively.

Most Organic Compound are Ox/Red in +3 to -3 V Range

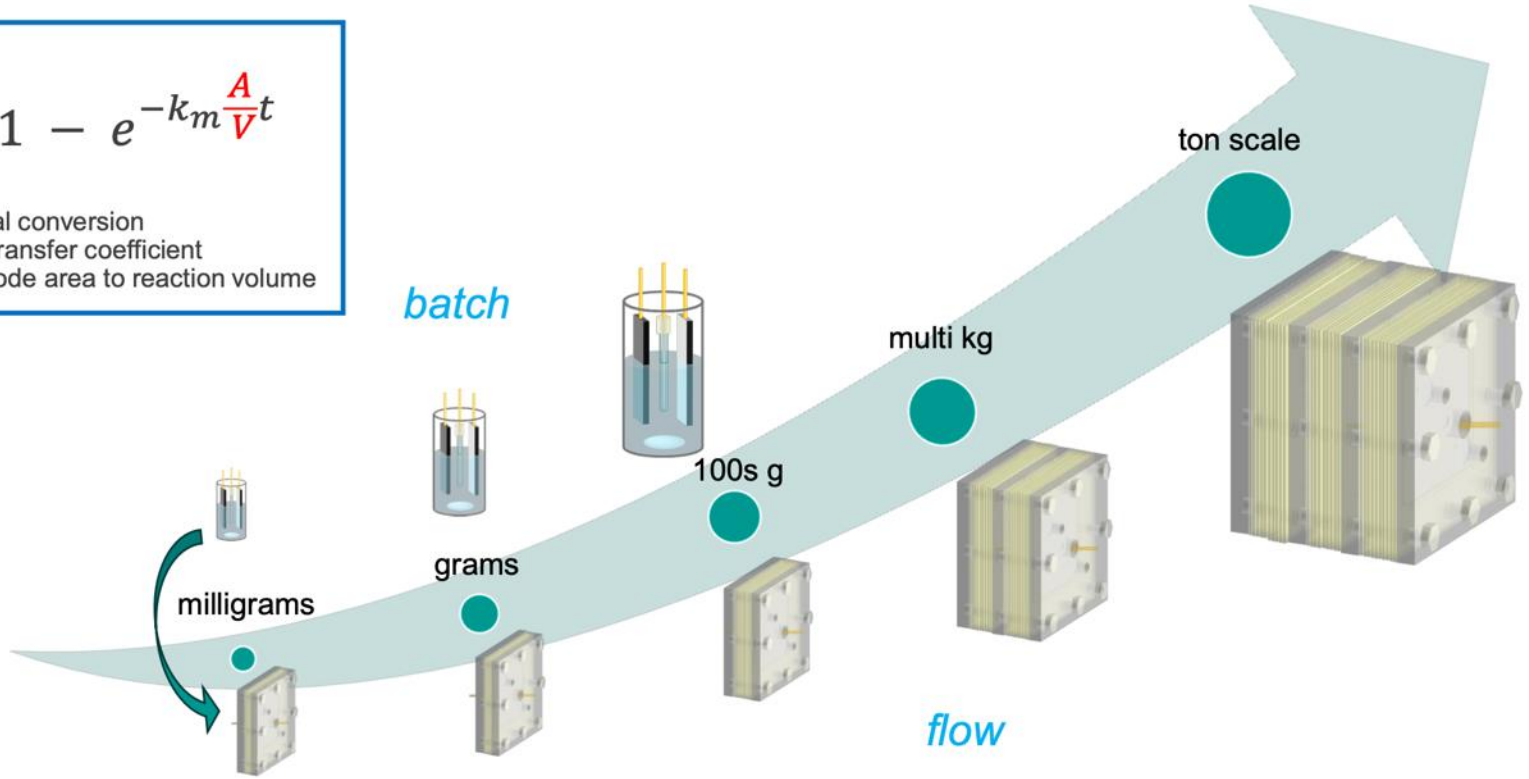
Slide: Prof. Ole Hammerich, Univ of Copenhagen

Electro Organic Chemistry

Electrochemistry Scale up

$$X = 1 - e^{-k_m \frac{A}{V} t}$$

X = fractional conversion
K_m = mass transfer coefficient
A/V = electrode area to reaction volume



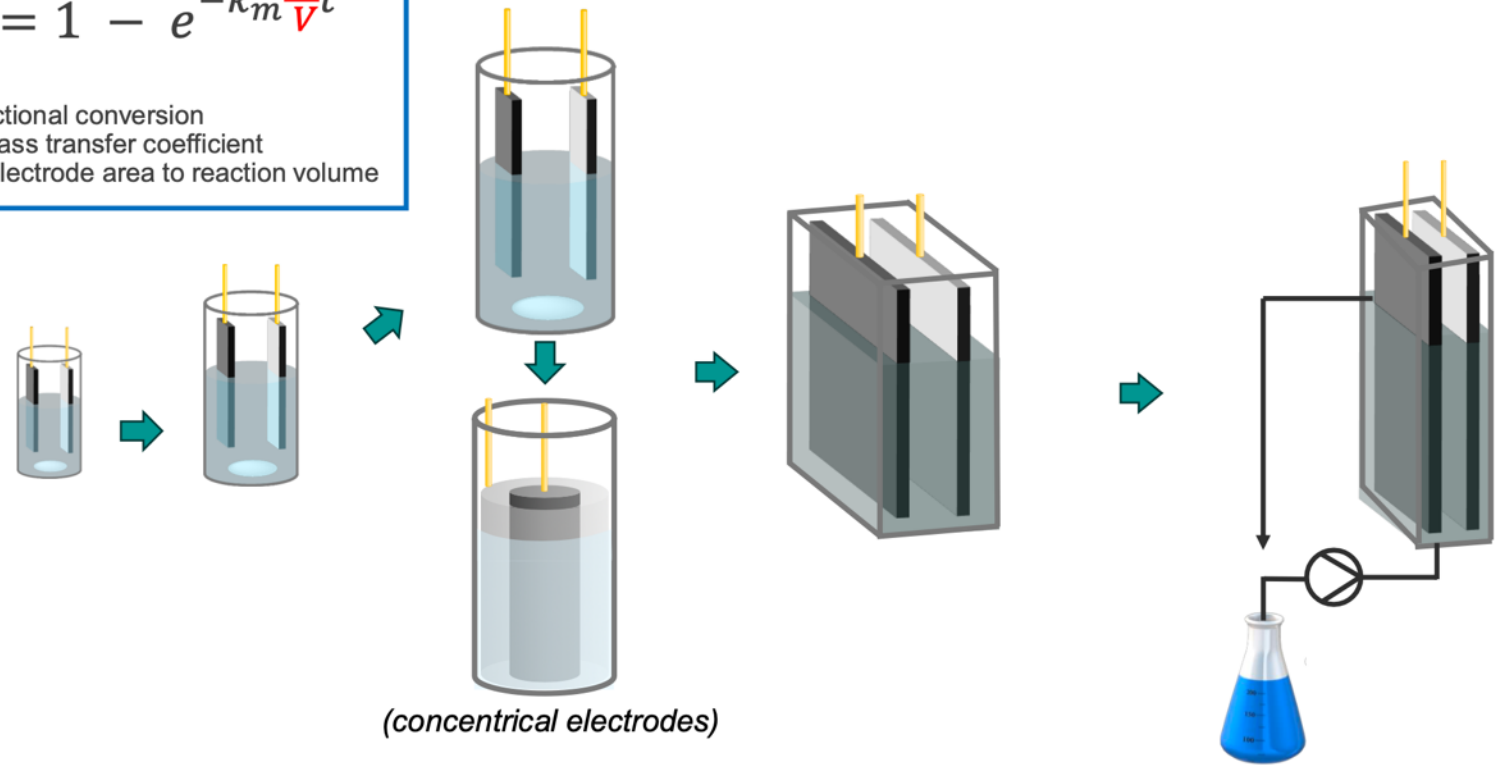
Slide: Prof. Cantillo, Univ of Queensland, Australia

Electro Organic Chemistry

What is Wrong with Batch Scale-Up?

$$X = 1 - e^{-k_m \frac{A}{V} t}$$

X = fractional conversion
K_m = mass transfer coefficient
A/V = electrode area to reaction volume

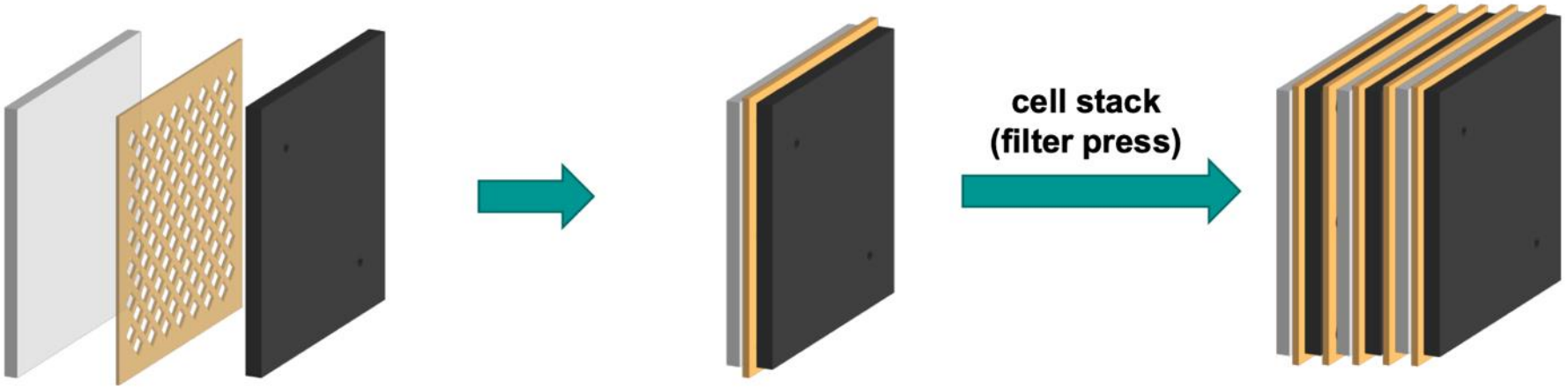


(concentrical electrodes)

Slide: Prof. Cantillo, Univ of Queensland, Australia

Electro Organic Chemistry

Electrochemistry Scale up



FLOW ELECTROCHEMISTRY

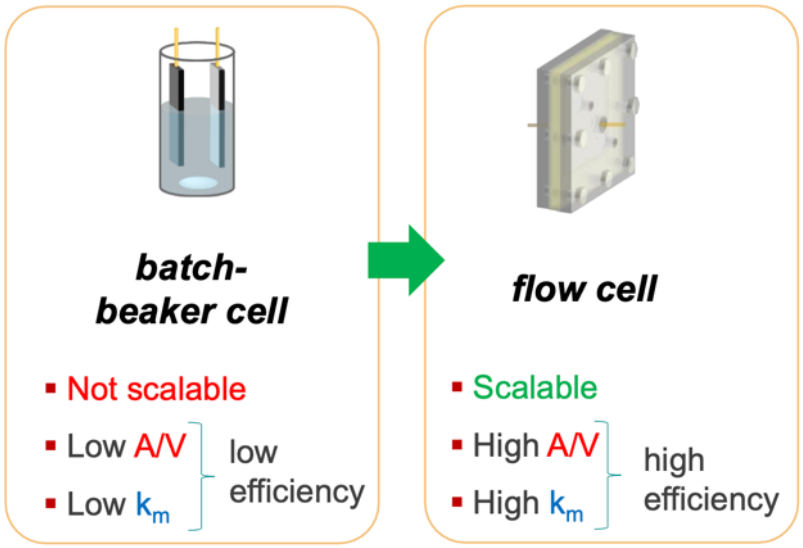
- SCALABLE
- electrodes distance: ideally < 1 mm
- minimization of supporting electrolyte
- very high electrode surface area to reactor volume ratio, which is independent of the electrode size

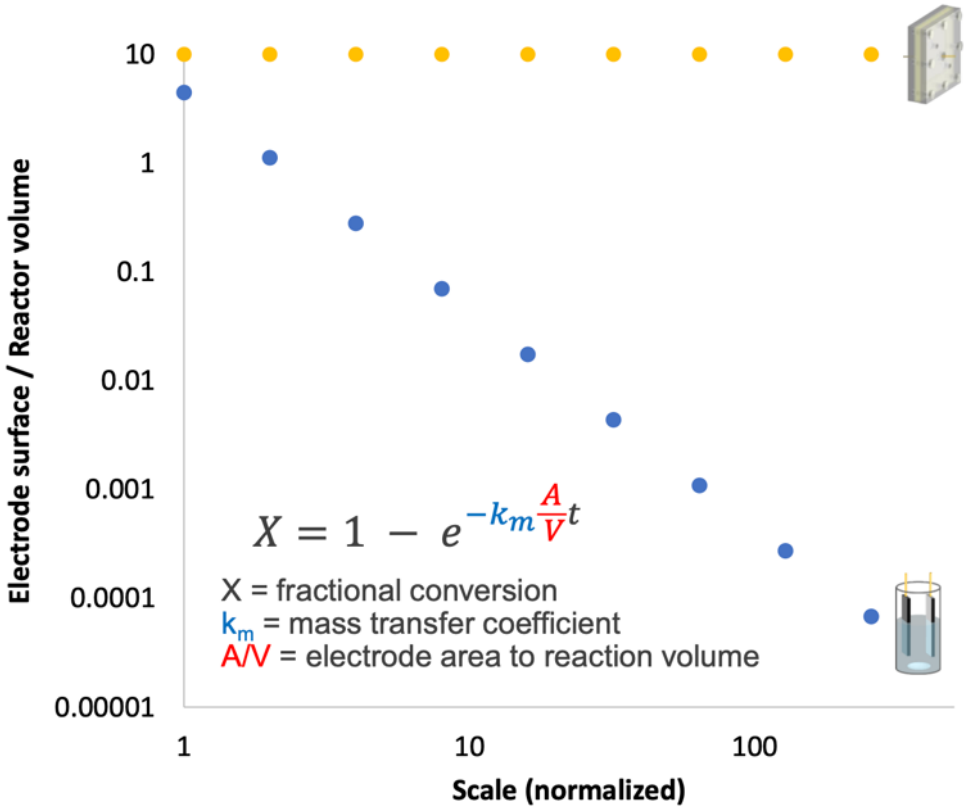
Slide: Prof. Cantillo, Univ of Queensland, Australia

Electro Organic Chemistry

Electrochemistry Scale up

Scale Up of Parallel Plate Flow Reactors





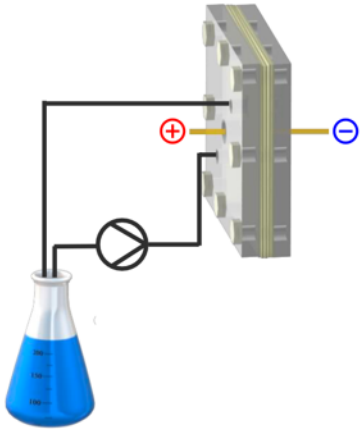
Slide: Prof. Cantillo, Univ of Queensland, Australia

Electro Organic Chemistry

Electrochemistry Scale up

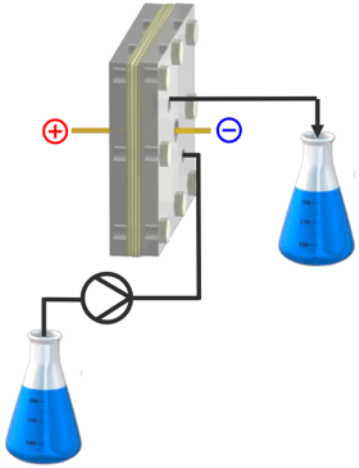
Flow Cell Operation

Recirculation



- Solution recirculated until high conversion is achieved
- High flow rates used
- Semi-batch process
- Development more simple than single-pass
- Gases can be easily released

Single-pass

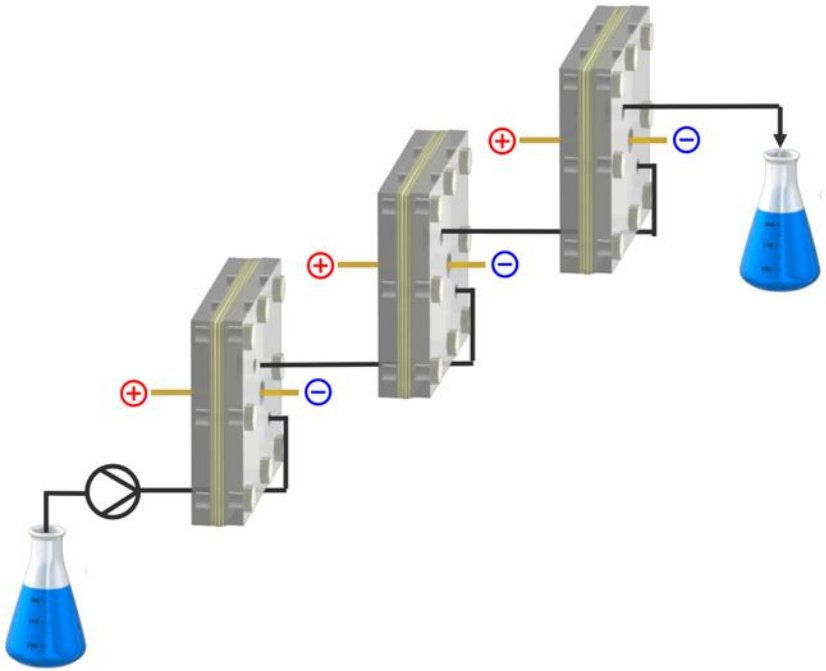


- High conversion in one pass through the cell
- Flow rate / current are adjusted
- Continuous process
- More challenging to develop
- Gas formation problematic

Slide: Prof. Cantillo, Univ of Queensland, Australia

Electro Organic Chemistry

Electrochemistry Scale up



Reactor Cascade

- Single-pass reactors in series
- Smaller conversion after each pass
- Opportunity for gas release
- Solution for reactions not reaching high conversion in a single-pass through a single-cell

Slide: Prof. Cantillo, Univ of Queensland, Australia

Electro Organic Chemistry

Basic Electrochemistry Calculations

Batch and Flow with Recirculation

reaction time: $t = \frac{F \cdot n \cdot z}{I}$

cell productivity: $\frac{n}{t} = \frac{I}{F \cdot z}$

Single-Pass Flow Processing

$t = \frac{F \cdot V \cdot C \cdot z}{I}$ ➡ flow rate: $\frac{V}{t} = \frac{I}{F \cdot C \cdot z}$

$F = 1608.0889 \frac{min \cdot mA}{mmol}$

F = Faradays's constant
n = amount substrate
C = substrate concentration

z = number of electrons (or $\frac{F}{mol}$)
I = current
V = volume

Continuous Flow Chemistry Lab

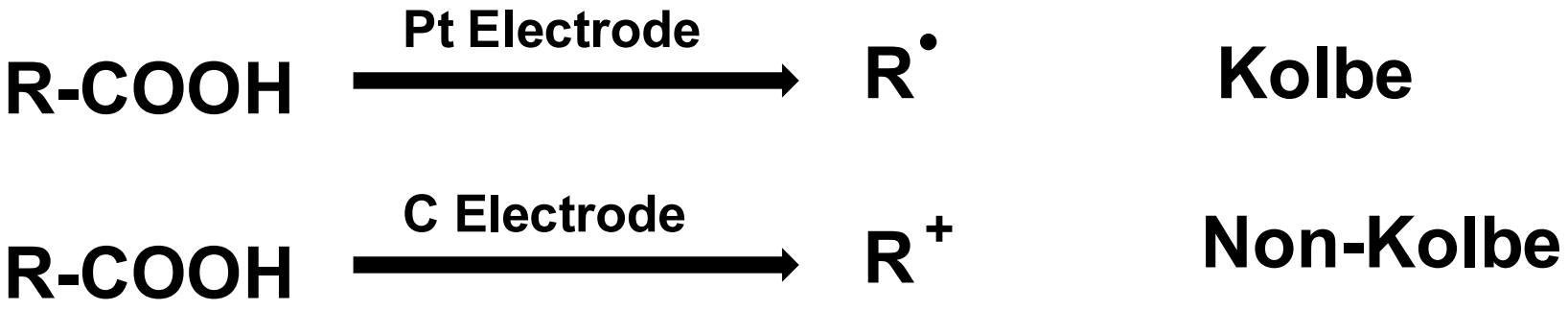
Electro Organic Chemistry

Why run reactions Electrochemically

- Greater precision over and redox potential range
- Polarity inversion is readily performed
- Heterogeneous reactions with different selectivity
- Ambient conditions
- Reactions can be started and stopped easily

Kolbe-Type Electro Organic Chemistry

Reactivity Control : Electrode Material



Kolbe:

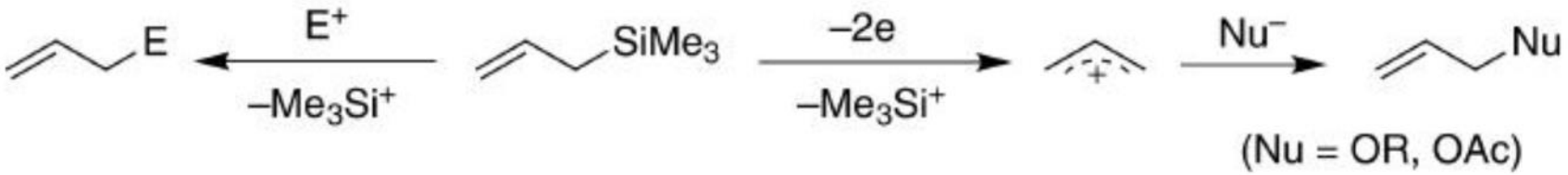
High Current Density
High Concentration
Weekly acidic or neutral conditions
No other anions
Non-Porous anodes (Pt or GC)

Fundamentals and applications of organic electrochemistry : synthesis, materials, devices / Toshio Fuchigami, Mahito Atobe, Shinsuke Inagi.

Electro Organic Chemistry

Reactivity Control

Umpolung without use of any reagents



Chemical Reactions

Alkyl Halides are Electrophiles: Grignard to convert them to Nucleophile

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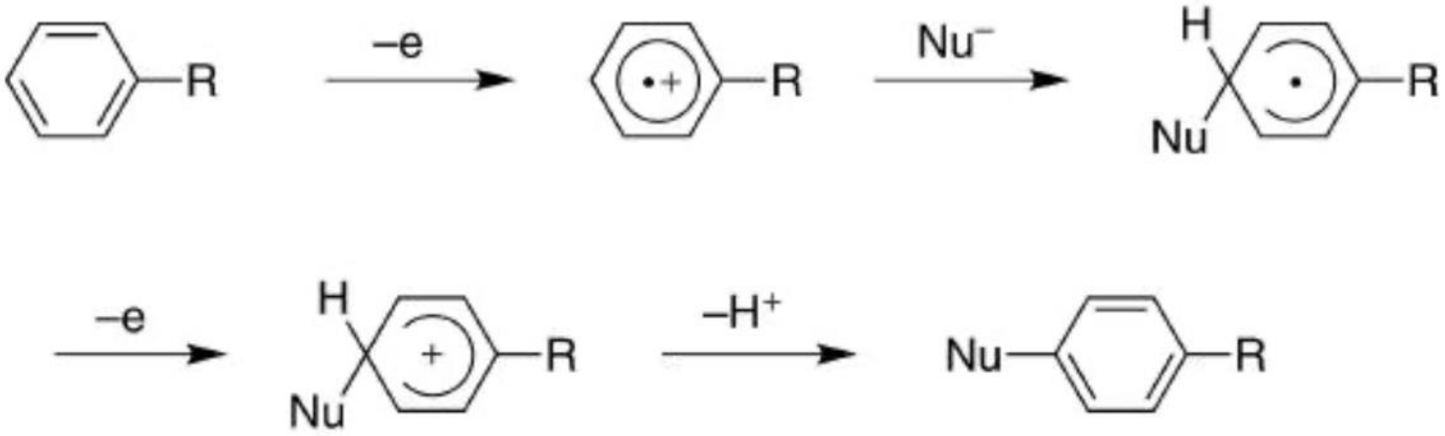
Electro Organic Chemistry

Reactivity Control

Umpolung without use of any reagents

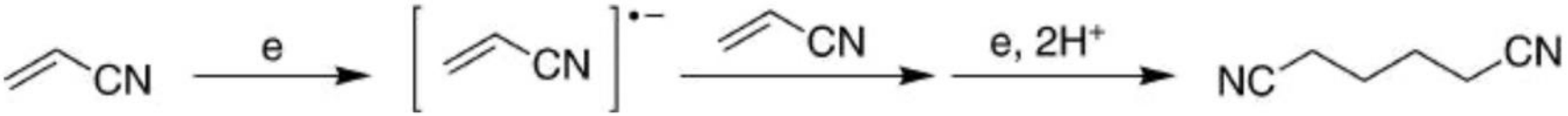


Fundamentals and applications of organic electrochemistry : synthesis, materials, devices / Toshio Fuchigami, Mahito Atobe, Shinsuke Inagi.

Electro Organic Chemistry

Reactivity Control

Umpolung without use of any reagents



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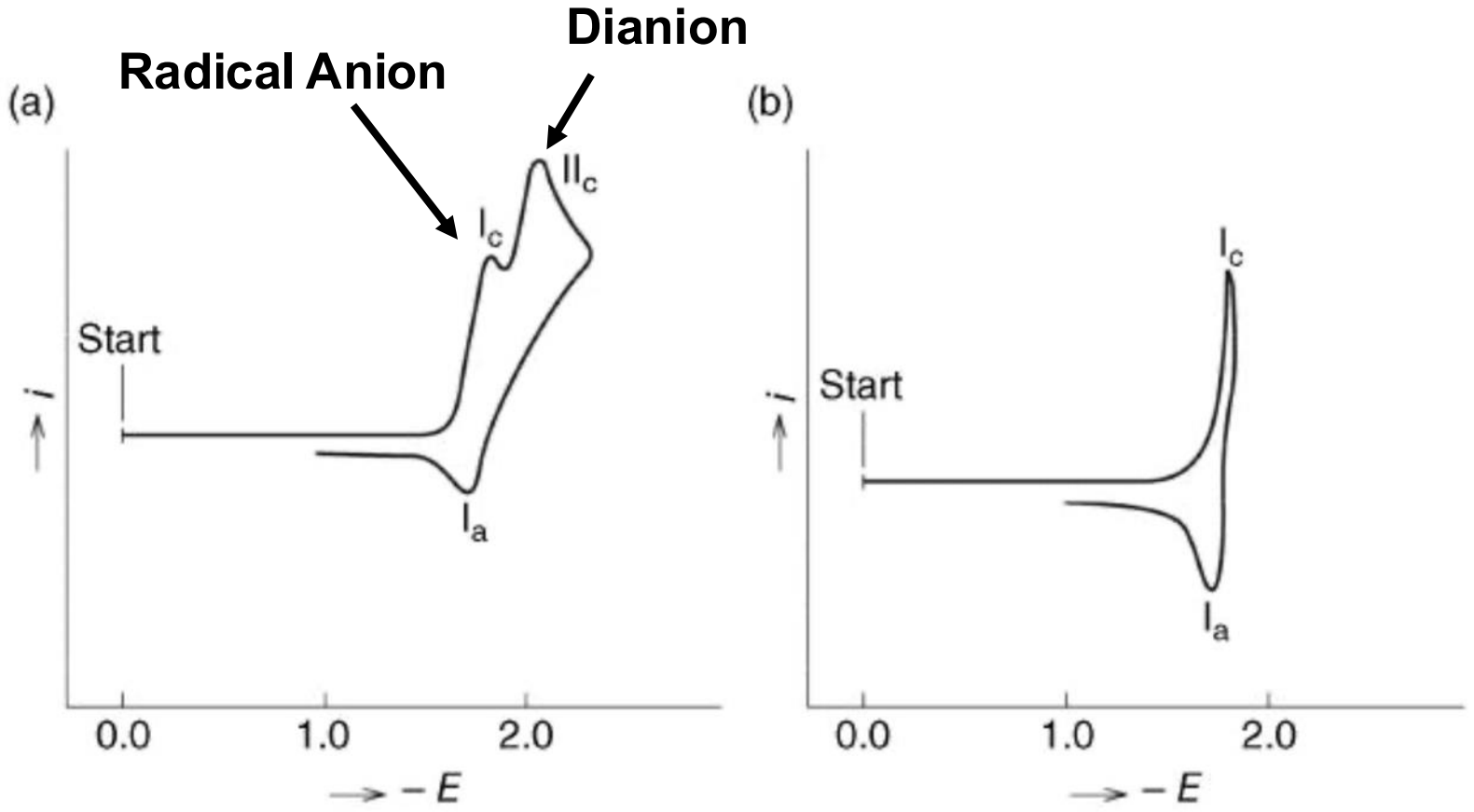
Electro Organic Chemistry

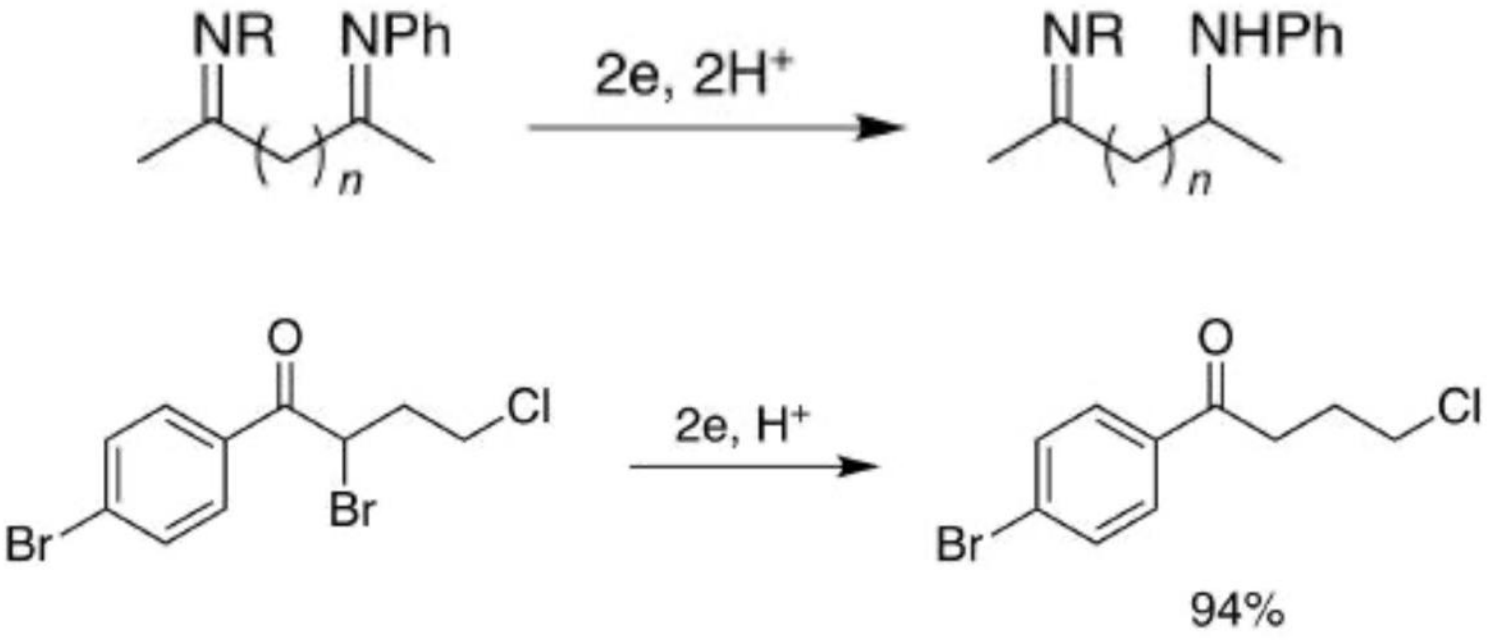
Reactivity Control : Benzophenone Reduction



Fundamentals and applications of organic electrochemistry : synthesis, materials, devices / Toshio Fuchigami, Mahito Atobe, Shinsuke Inagi.

Electro Organic Chemistry

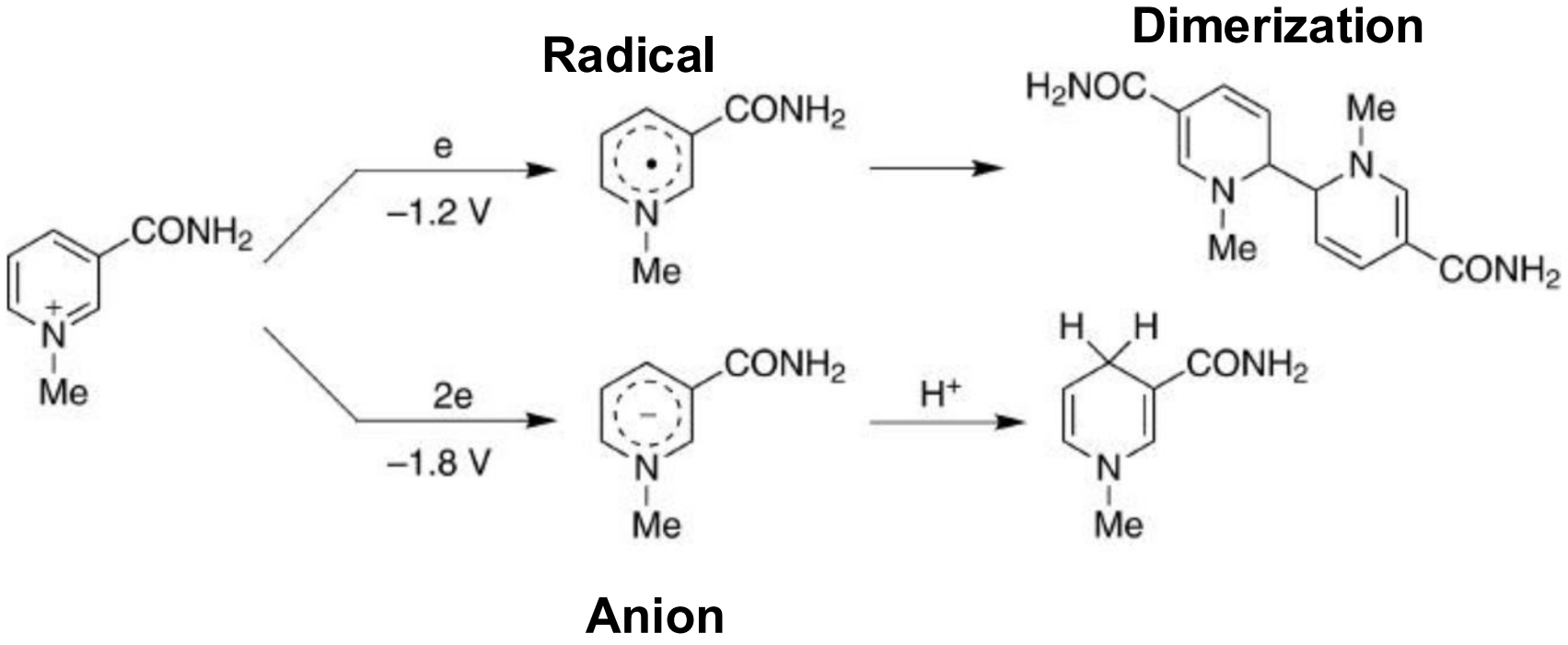
Reactivity Control : Chemoselectivity



Fundamentals and applications of organic electrochemistry : synthesis, materials, devices / Toshio Fuchigami, Mahito Atobe, Shinsuke Inagi.

Electro Organic Chemistry

Reactivity Control : Reaction Pathway Selectivity



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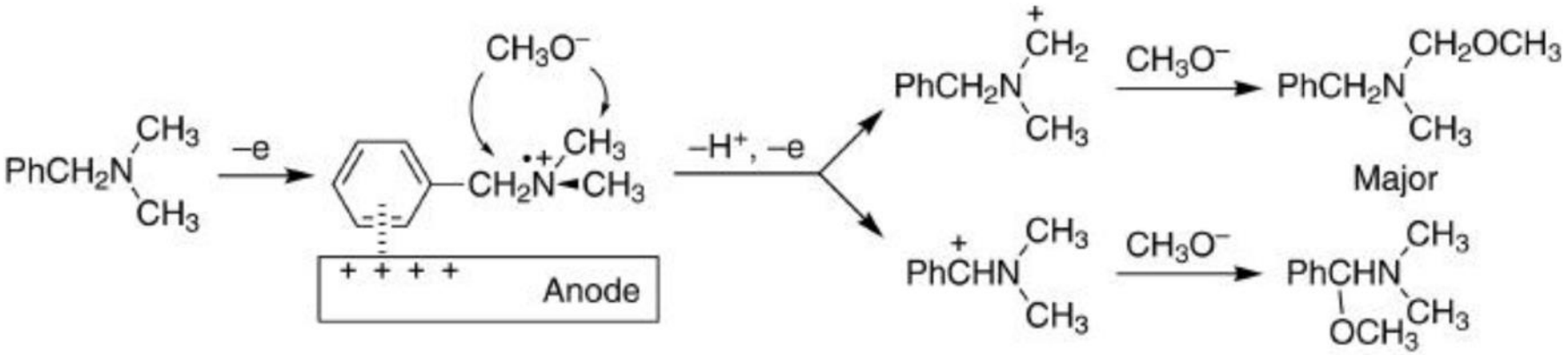
Electro Organic Chemistry

Reactivity Control : Reaction Pathway Selectivity



Kinetic Control:

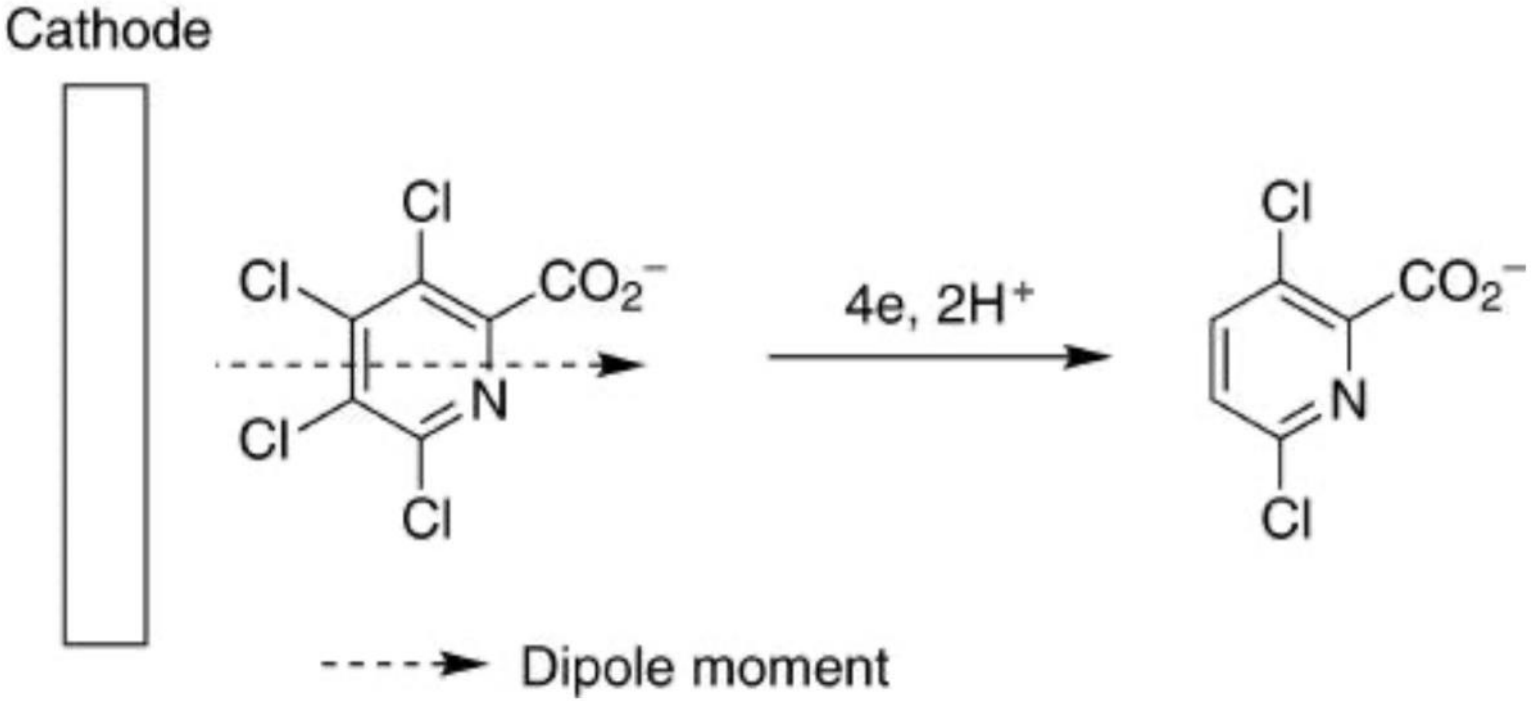
The anodically generated radical cation intermediate seems to be adsorbed on the anode, deprotonation takes place preferentially from a less hindered methyl group (also cation formation farthest from anode is favored).

Fundamentals and applications of organic electrochemistry : synthesis, materials, devices / Toshio Fuchigami, Mahito Atobe, Shinsuke Inagi.

Electro Organic Chemistry

Reactivity Control :

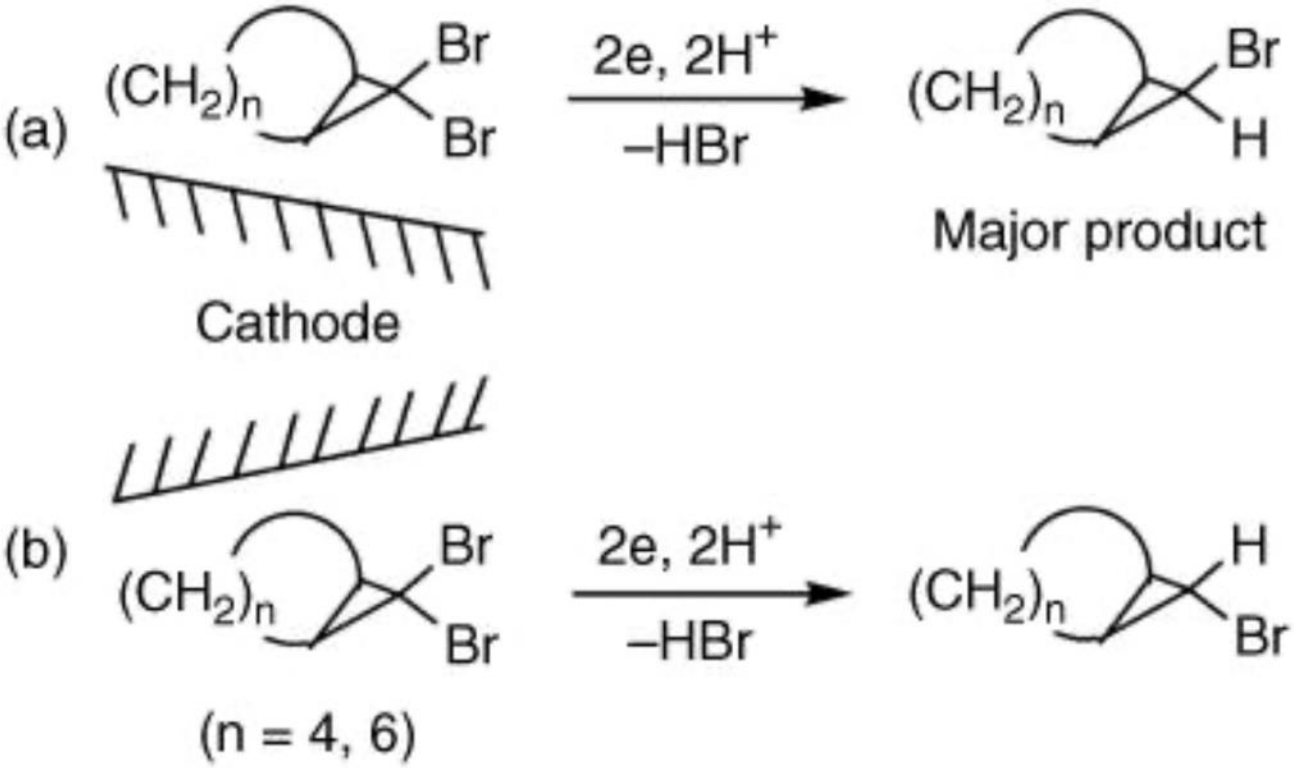
Selective Adsorption due to its Dipole Moment



Fundamentals and applications of organic electrochemistry : synthesis, materials, devices / Toshio Fuchigami, Mahito Atobe, Shinsuke Inagi.

Electro Organic Chemistry

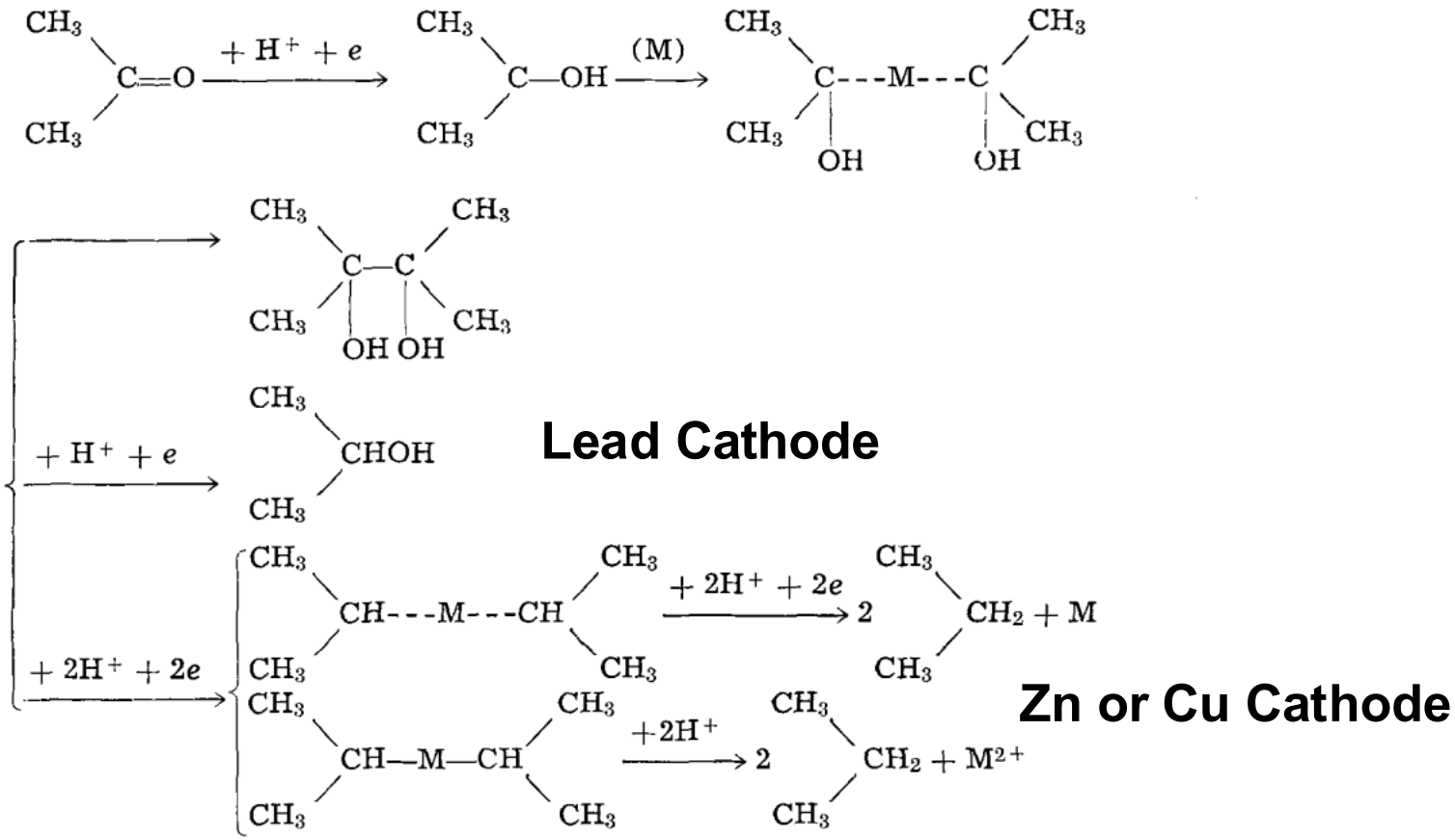
Reactivity Control : *Steric Hindrance*



Fundamentals and applications of organic electrochemistry : synthesis, materials, devices / Toshio Fuchigami, Mahito Atobe, Shinsuke Inagi.

Electro Organic Chemistry

Reactivity Control : Electrode Material



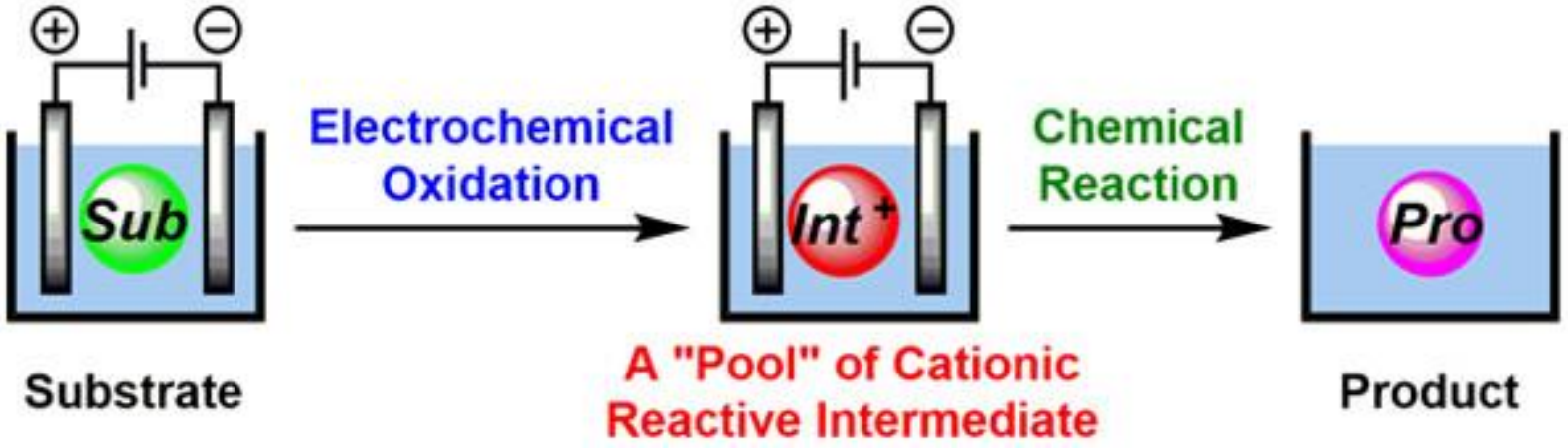
Lead Cathode

Zn or Cu Cathode

Taro Sekine et al 1965 J. Electrochem. Soc. 112 439

Electro Organic Synthesis

Electrogenerated Cationic Reactive Intermediates

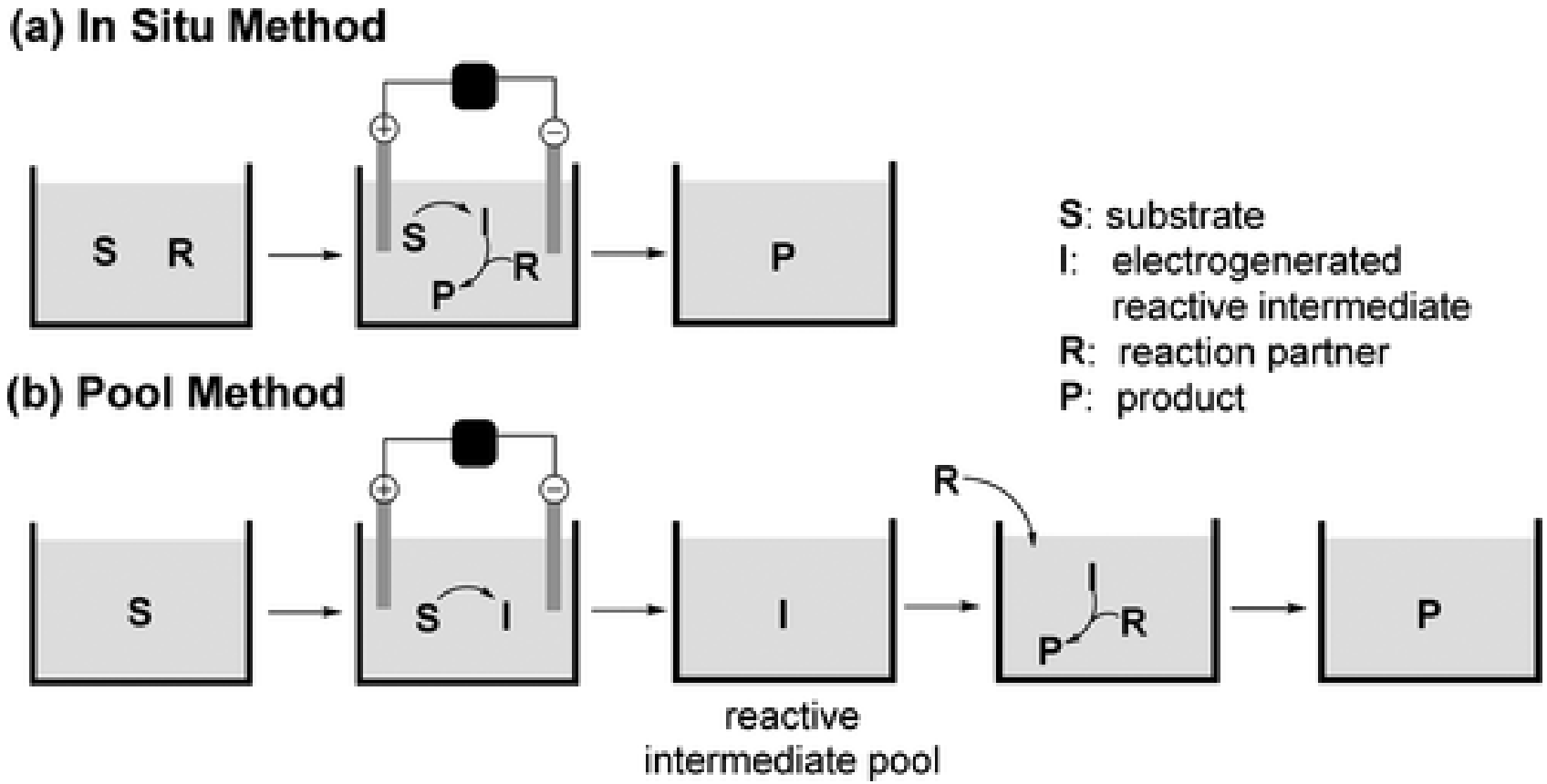


Prof. Dr. Jun-ichi Yoshida
(1952–2019)

Yoshida and coworkers, Chem. Rev. 2018, 118, 4702

Electro Organic Synthesis

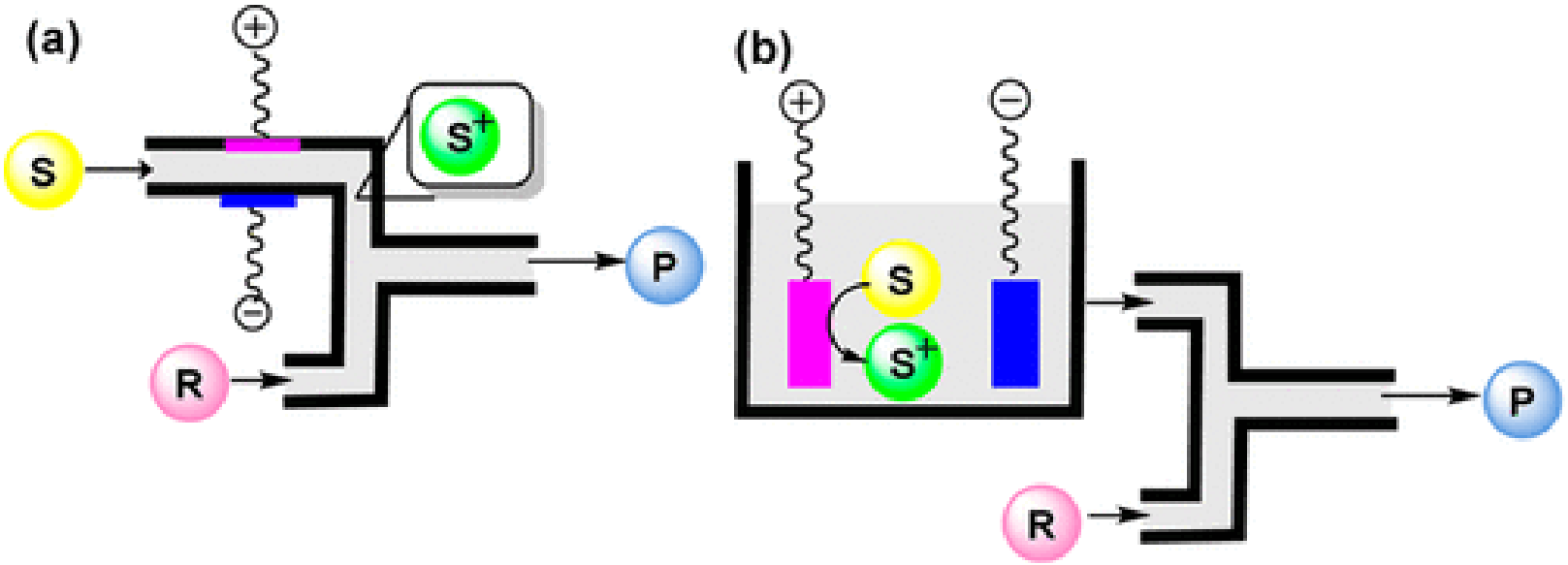
Electrogenerated Cationic Reactive Intermediates



Yoshida and coworkers, Chem. Rev. 2018, 118, 4702

Electro Organic Synthesis

Electrogenerated Cationic Reactive Intermediates

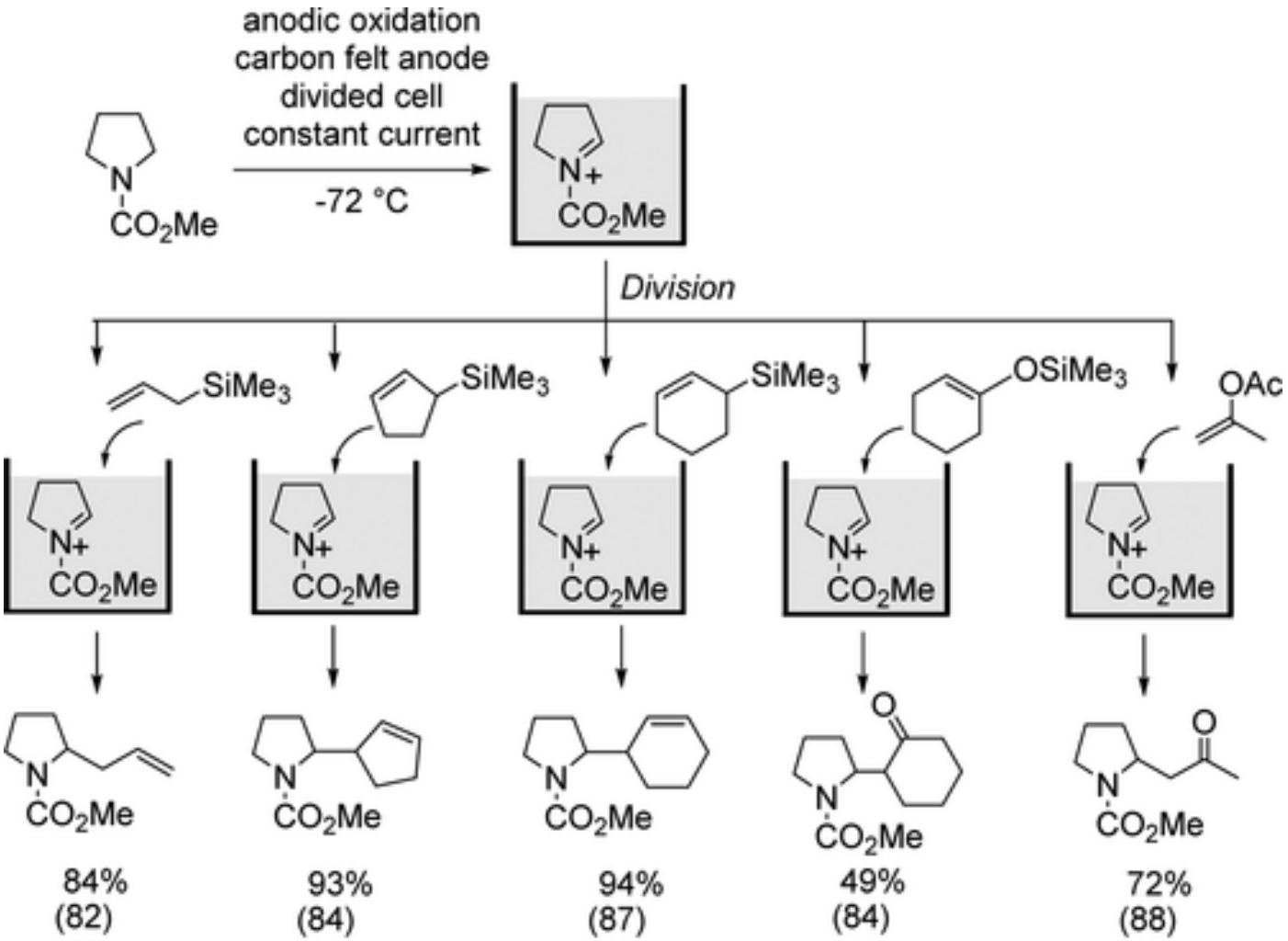


Combining Electro and Flow

Yoshida and coworkers, Chem. Rev. 2018, 118, 4702

Electro Organic Synthesis

Electrogenerated Cationic Reactive Intermediates

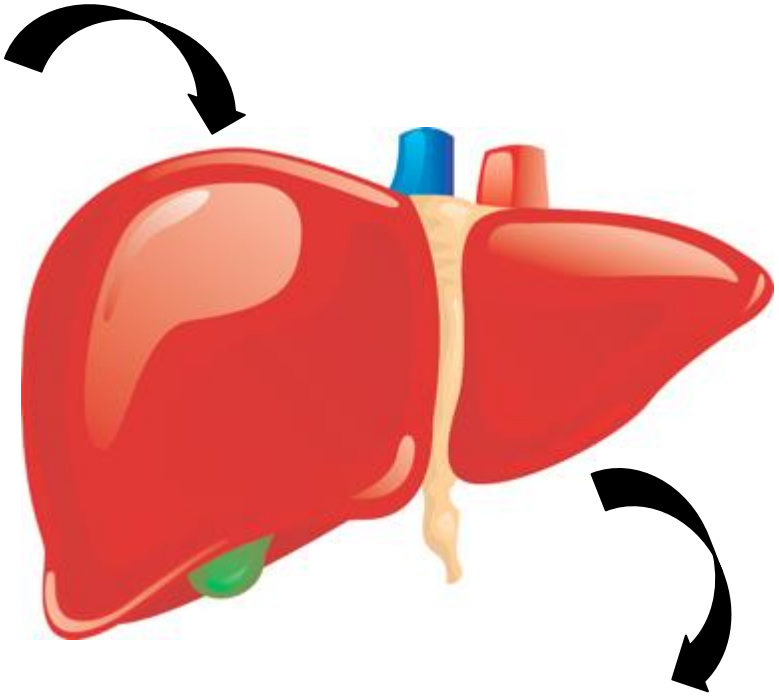


Yields in parentheses were obtained with manual operation.

Yoshida and coworkers, Chem. Rev. 2018, 118, 4702

CF Electrosynthesis: Drug Discovery

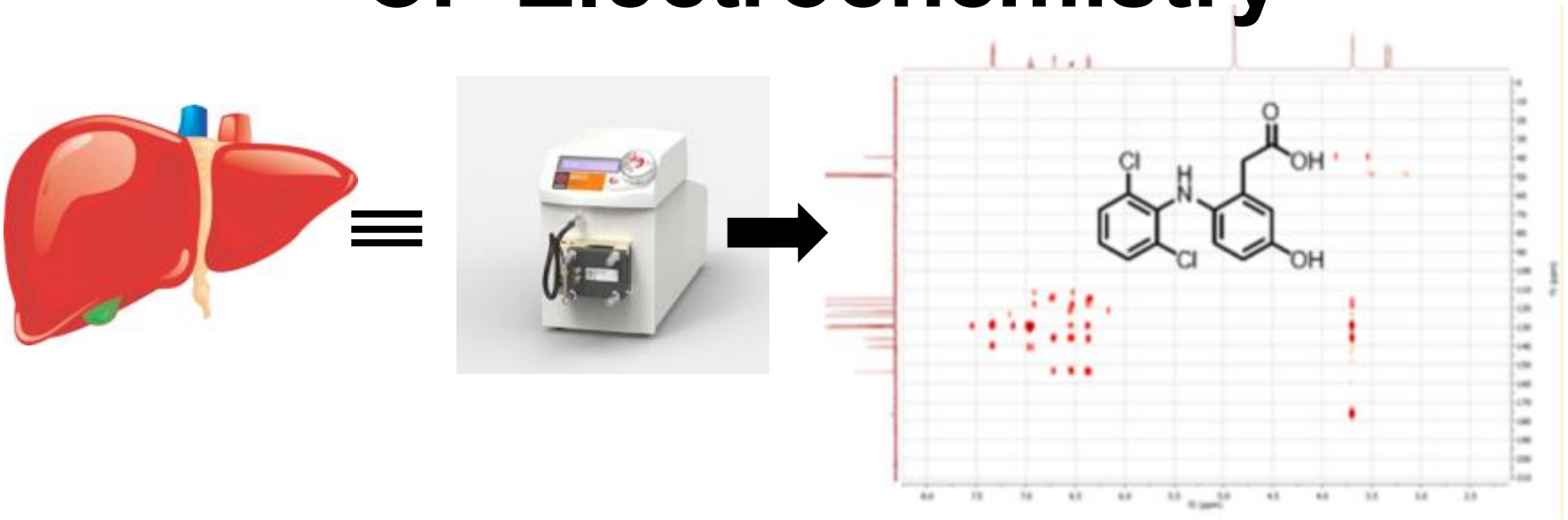
DRUG

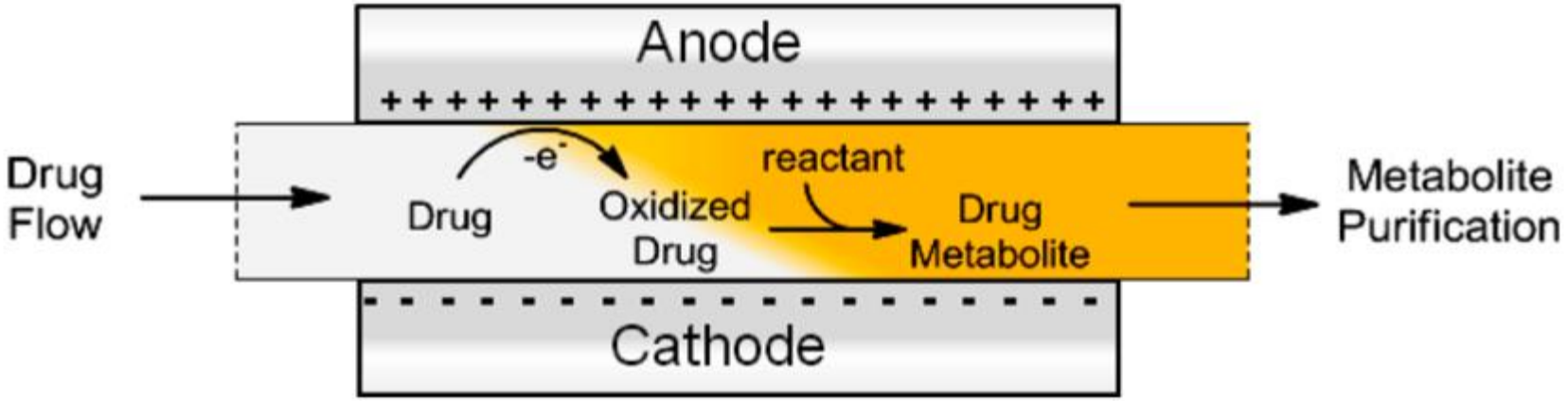


Oxidation (Phase 1)
Drug Metabolites

Stalder and Roth; ACS Med. Chem. Lett. 2013, 4, 1119−1123

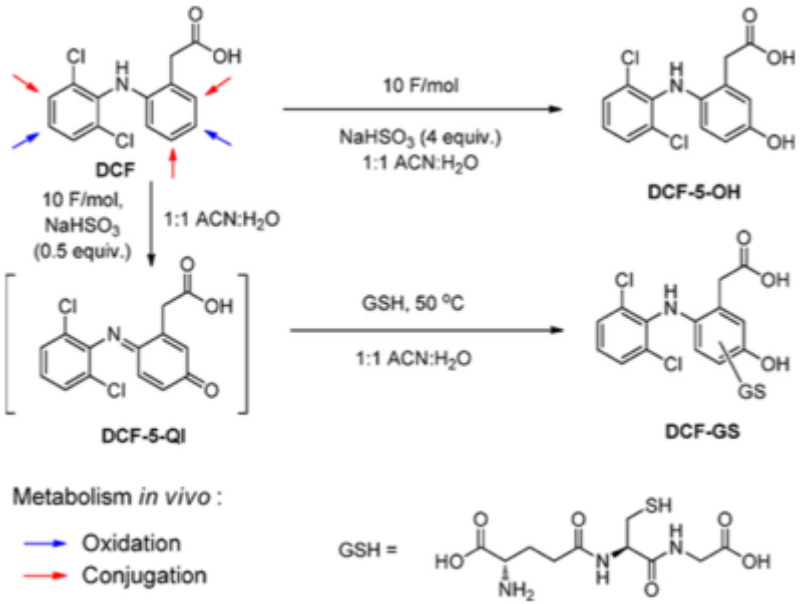
CF Electrochemistry

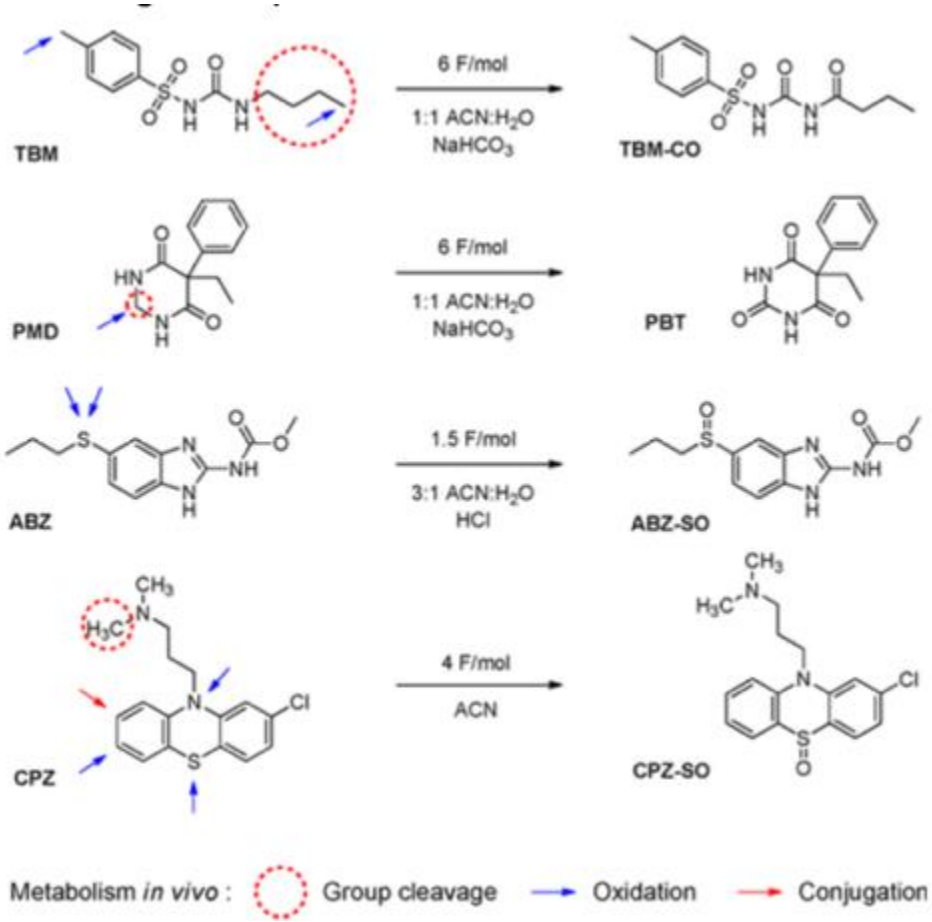




Stalder and Roth; ACS Med. Chem. Lett. 2013, 4, 1119−1123

Electrosynthesis of Phase I Metabolite





Diclofenac (DCF-5-OH)

Stalder and Roth; ACS Med. Chem. Lett. 2013, 4, 1119−1123

Continuous Flow Chemistry Lab

Industrial Electrochemical Processes

Challenges and Opportunities

Industrial Electrochemical Processes

Major Players in Electro Organic Synthesis:

USA: 3M, Dow, Olin, Electrosynthesis and Reilly Chemical

Canada: Albright and Wilson, Noranda and Hydro Quebec

Europe: Isochem, Sorapec in France,
BASF and Clariant in Germany,
Akzo Nobel in The Netherlands

Japan: Asahi Chemical, Otsuka Chemical, Tokyo Carbon,
Tokai and Tosoh

Industrial Electrochemical Processes

Starting material	Product	Company
Butanone	Acetoin (3-hydroxybutanone)	BASF
1,4-Butynediol	Acetylenedicarboxylic Acid	BASF
Acrylonitrile (hydrodimerization)	Adiponitrile (> 200.000 tons/year) (production of nylon 66)	Monsanto, BASF, Asahi Chemical
4-Cyanopyridine	4-Aminomethylpyridine	Reilly Tar
Anthracene	Anthraquinone	L. B. Holliday, ECRC
Nitrobenzene	Azobenzene	Several
Glucose	Calcium Gluconate	Sandoz, India
L-Cystine	L-Cysteine	Several
Diacetone-L-sorbose	Diacetone-2-ketogulonic Acid	Hoffman-LaRoche
Naphthalene	1,4-Dihydronaphthalene	Hoechst

Industrial Electrochemical Processes

Starting material	Product	Company
Furan	2,5-Dimethoxy-2,5-dihydrofuran	BASF
Monomethyladipate	Dimethylsebacate	Asahi Chemical
Hexafluoropropylene	Hexafluoropropyleneoxide	Hoechst
m-Hydroxybenzoic Acid	*m*-Hydroxybenzyl Alcohol	Otsuka
Galacturonic Acid	Mucic Acid	EDF
Hydrocarbons	Perfluorinated hydrocarbons	3M, Bayer, Hoechst
p-Methoxytoluene	*p*-Methoxybenzaldehyde	BASF
p-tert-Butyltoluene	*p-tert*-Butylbenzaldehyde	BASF, Givaudan
o-Hydroxybenzoic Acid	Salicylic Aldehyde	India
Maleic Acid	Succinic Acid	CERCI, India

Industrial Electrochemical Processes

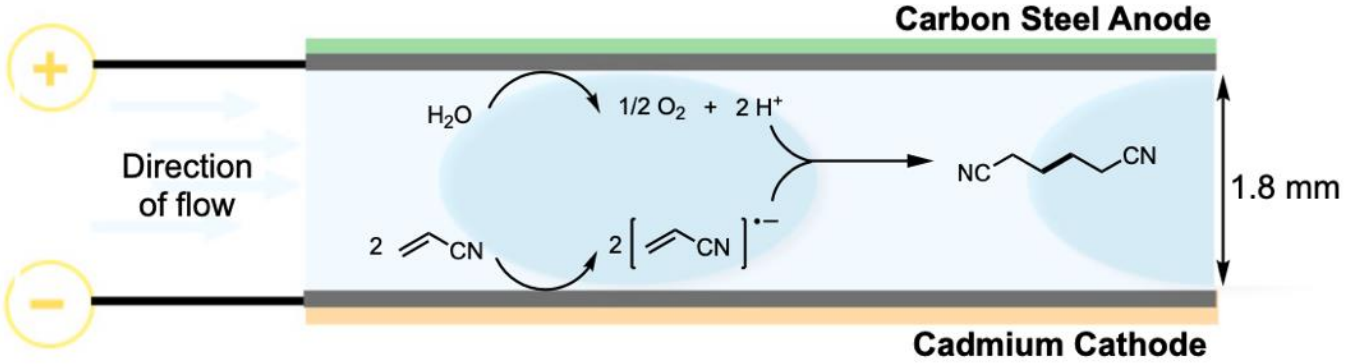
Inorganic Chemicals

Chemical	Equation[a]	Anode (A) Cathode (C)	Conditions
Aluminium[24]	$2\,Al_2O_3 + 3\,C \rightarrow 4\,Al + 3\,CO_2$ $E_0 = -1.16$ V (1010 °C)	Carbon (A) Aluminium (C)	Molten cryolite, Al_2O_3; 1000 °C; 1 A cm^{-2}; 4.3 V
Chlorine/ Caustic soda[25]	$2\,NaCl\,(aq) + 2\,H_2O \rightarrow$ $Cl_2\,(g) + H_2\,(g) + 2\,NaOH$ $E_0 = -1.36$ V	Noble Metal Oxide/Ti (A) Steel or Hg (C)	Aqueous NaCl; asbestos or ion-exchange membrane; 80-95 °C; 200-1000 mA cm^{-2}
Chloride[25] Na^+	$2\,Cl^- \rightarrow Cl_2 + 2\,e^-$ $E^0 = 1.36$ V $2\,H_2O + 2\,e^- \rightarrow 2\,OH^- + H_2$ $E^0 = 0.0$ V $2\,HOCl + OCl^- \rightarrow ClO_3^- + 2\,Cl^- + 2\,H^+$	Noble Metal Oxide/Ti (A) Steel (C)	Aqueous NaCl (310 g dm^{-3}); $Na_2Cr_2O_7$ (1-6 g dm^{-3}); 60-80 °C; 150-400 mA cm^{-2}
Perchlorate[26] Na^+, NH_4^+	$ClO_3^- + H_2O \rightarrow ClO_4^- + 2\,H^+ + 2\,e^-$ $E^0 = 1.19$ V	Pt/Ti, PbO_2/Graphite (A) Steel or Ni (C)	Aqueous ClO_3^-; $Na_2Cr_2O_7$; 35-50 °C; 150-500 mA cm^{-2}
Persulphate[27] Na^+, NH_4^+, H^+	$2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2\,e^-$ $E^0 = 2.01$ V	Pt or Pt/Ti (A)	Conc. H_2SO_4, cold; 500-1000 mA cm^{-2}; divided cell
Permanganate,[28] K^+	$MnO_4^{2-} \rightarrow MnO_4^- + e^-$ $E^0 = 0.54$ V	Ni, Monel (A) Fe or Steel (C)	K_2MnO_4 (25-100 g dm^{-3}) 1-4 mol L^{-1} aq. KOH at 60 °C; 5-150 mA cm^{-2}; undivided cell
Fluorine[18]	$2\,F^- \rightarrow F_2 + 2\,e^-$ $E^0 = 2.87$ V	Carbon (A) Mild steel (C)	KF-2HF (eutectic) at 82 °C; 13 mA cm^{-2}; undivided cell (skirt)
Manganese[18] Dioxide	$Mn^{2+} + 2\,H_2O \rightarrow MnO_2 + 4\,H^+ + 2\,e^-$ $E^0 = 1.23$ V	Graphite, Pb or Ti (A)	$MnSO_4$ (0.5-1.2 mol L^{-1}) in aq. H_2SO_4 at 90-100 °C; 7-12 mA cm^{-2}; undivided cell
Water Electrolysis[29]	$2\,H_2O + 2\,e^- \rightarrow H_2 + 2\,OH^-$ $E^0 = 0.0$ V $2\,OH^- \rightarrow O_2 + 2\,H^+ + 4\,e^-$ $E^0 = 1.23$ V	Ni plated on steel (A) Steel (C)	Aq. KOH (25-30 wt.%) at 70 °C; divided cell (asbestos)
Hydrogen Peroxide[26]	$O_2 + H_2O + 2\,e^- \rightarrow HO_2^- + OH^-$ $HO_2^- + H_2O \rightarrow H_2O_2 + OH^-$ $E^0 = 0.68$ V	Graphite or carbon (C)	1 mol L^{-1} aq. NaOH, cold; 25-150 mA cm^{-2}; divided cell
Ozone[18]	$O_2 + H_2O \rightarrow O_3 + 2\,H^+ + 2\,e^-$ $E^0 = 2.07$ V	Vitreous carbon (A)	Conc. aq. HBF_4, cold; 500 mA; divided cell

Electro Organic Synthesis

Baizer Process (Monsanto): >3,00,000 tons/yr

The New Monsanto Process:

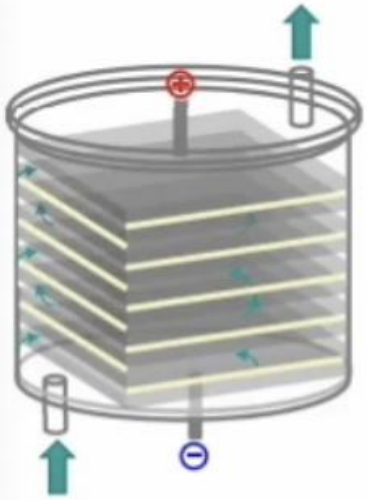


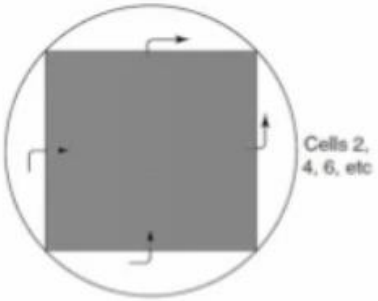
	1965 Monsanto Process	1984 New Monsanto Process
Reactor type	Stirred tank	Plug flow
Cell type	Divided	Undivided
Adiponitrile selectivity (%)	92	88
Inter-electrode gap (cm)	0.7	0.18
Electrolyte resistivity (Ω cm)	38 (catholyte)	12
Current density (A/cm^2)	0.45	0.20
Supporting electrolyte (%)	40	15.4
Production (ton/year)	900	~ 3×10^5
Energy consumption (kWh/ton)	6700	2500

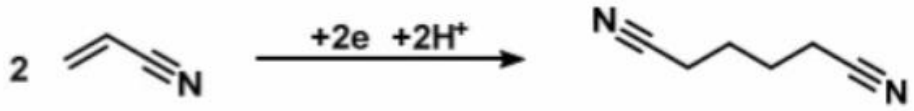
iScience 23, 101720, November 20, 2020

Electro Organic Synthesis

Baizer Process (Monsanto): >3,00,000 tons/yr







- Two phase aqueous phosphate buffer acrylonitrile
- Undivided bipolar parallel plate cell.
- Cd cathode
- Steel anode
- Current 200 mA/cm^2

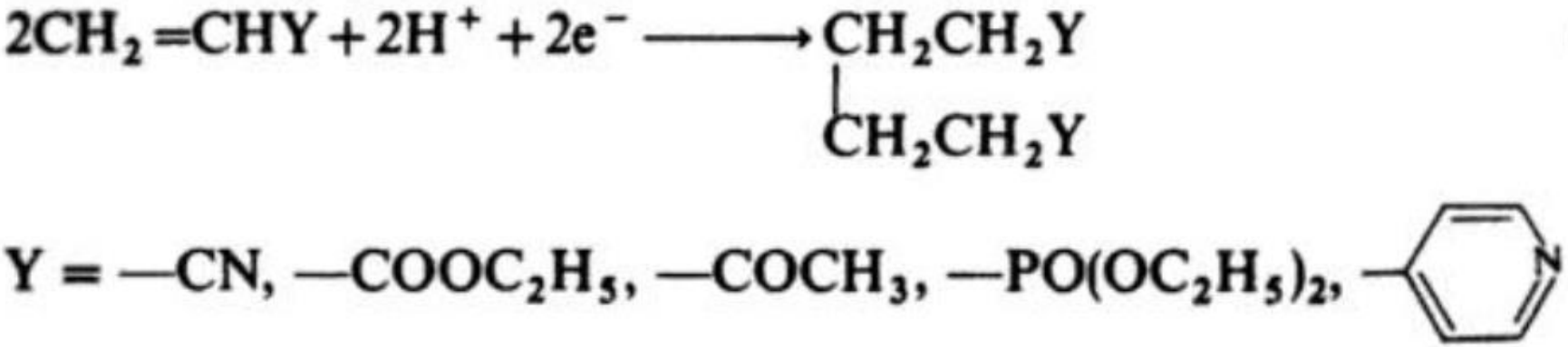
Cell

- Square flat electrode plates on cylindrical vessel
- Improved current distribution
- Isolating frames avoid current bypass in bipolar plates

Chem. Ing. Tech. 2005, 77, 1363

Electro Organic Synthesis

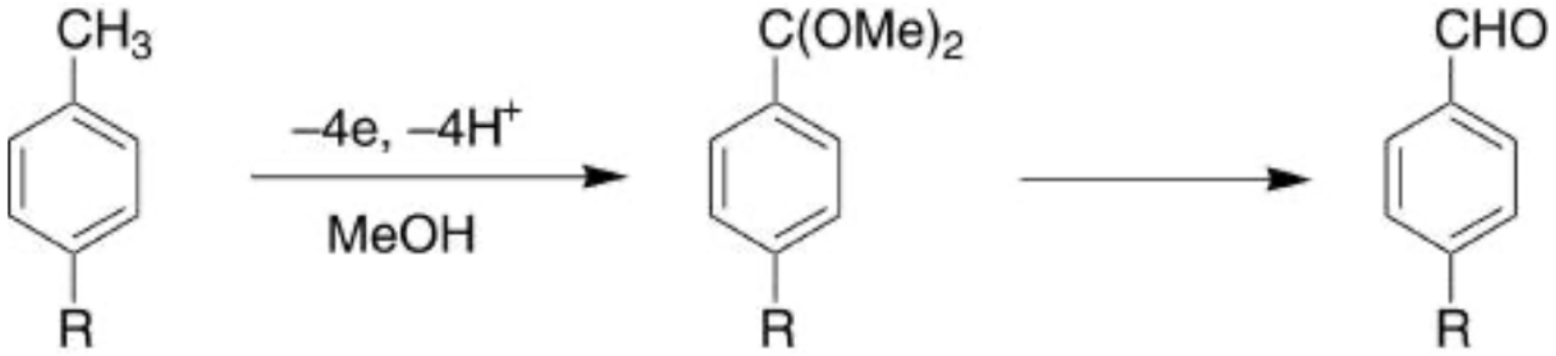
Baizer Process (Monsanto): >3,00,000 tons/yr



Electro Organic Synthesis

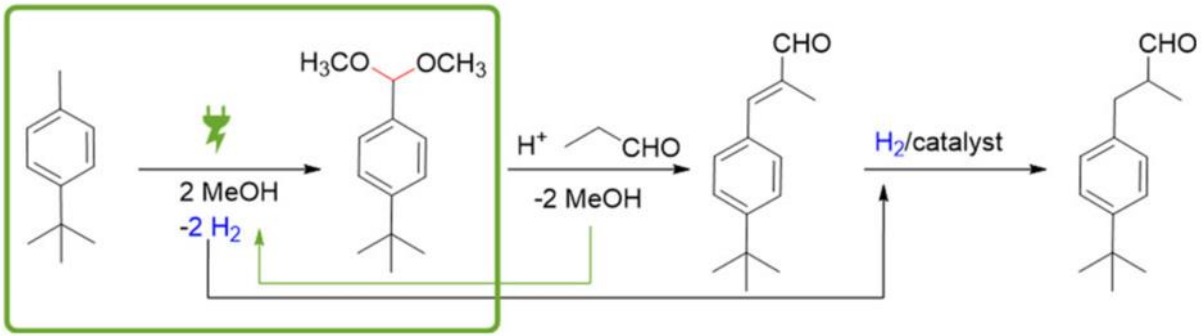
Electrosynthesis of Aromatic Aldehydes

BASF Process



Electro Organic Synthesis

Lysmeral Process (BASF): >10,000 tons/yr



Bipolar packed electrode stack, which is called capillary gap cell.
Graphite disk electrode at 50 C
Current Density of 42 mA/cm^2
Selectivity 91% and Yield 78%
Current Efficiency of 70%
Cell Voltage 4 V
EEC of 2.94 kWh/kg

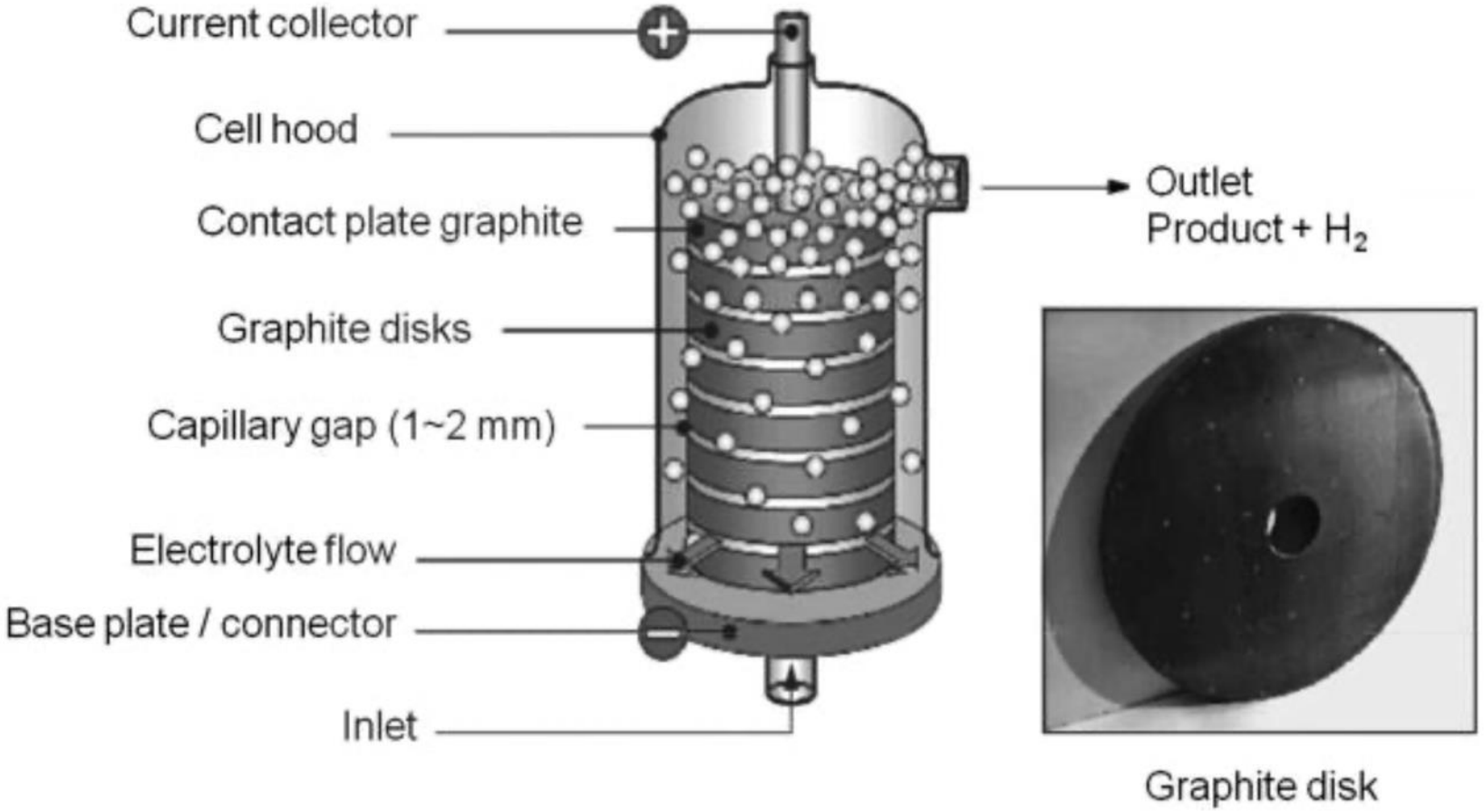
Electric Energy cost = 0.1 Euro kWh
1Kg Lysmeral = 0.29 Euro (Excluding work up)

Extended for Anisaldehyde

Chem. Ing. Tech. 2005, 77, 1363

Electro Organic Synthesis

Lysmeral Process (BASF)



Chem. Ing. Tech. 2005, 77, 1363

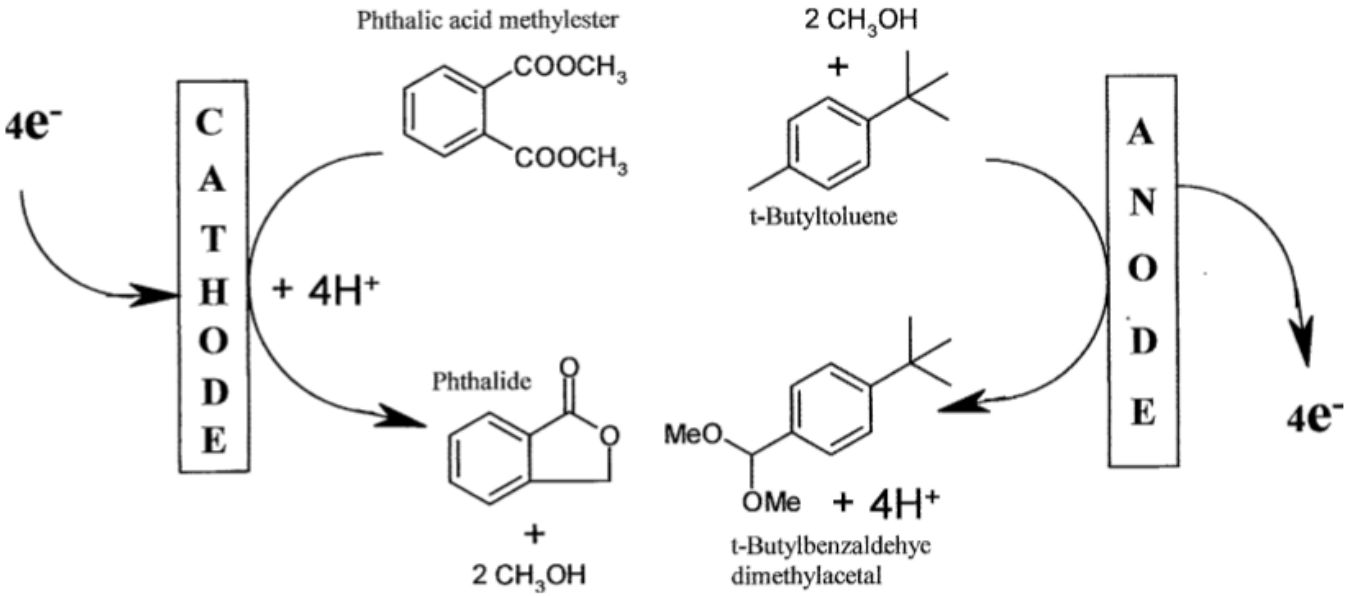
Electro Organic Synthesis

Lysmeral Process (BASF)

Chem. Ing. Tech. 2005, 77, 1363

Electro Organic Synthesis

New Process (BASF in 1990's)



Bipolar packed electrode stack, which is called capillary gap cell.

Graphite disk electrode at 50 C

Current Density of 100 mA/cm^2

Yield 180 % (90% each)

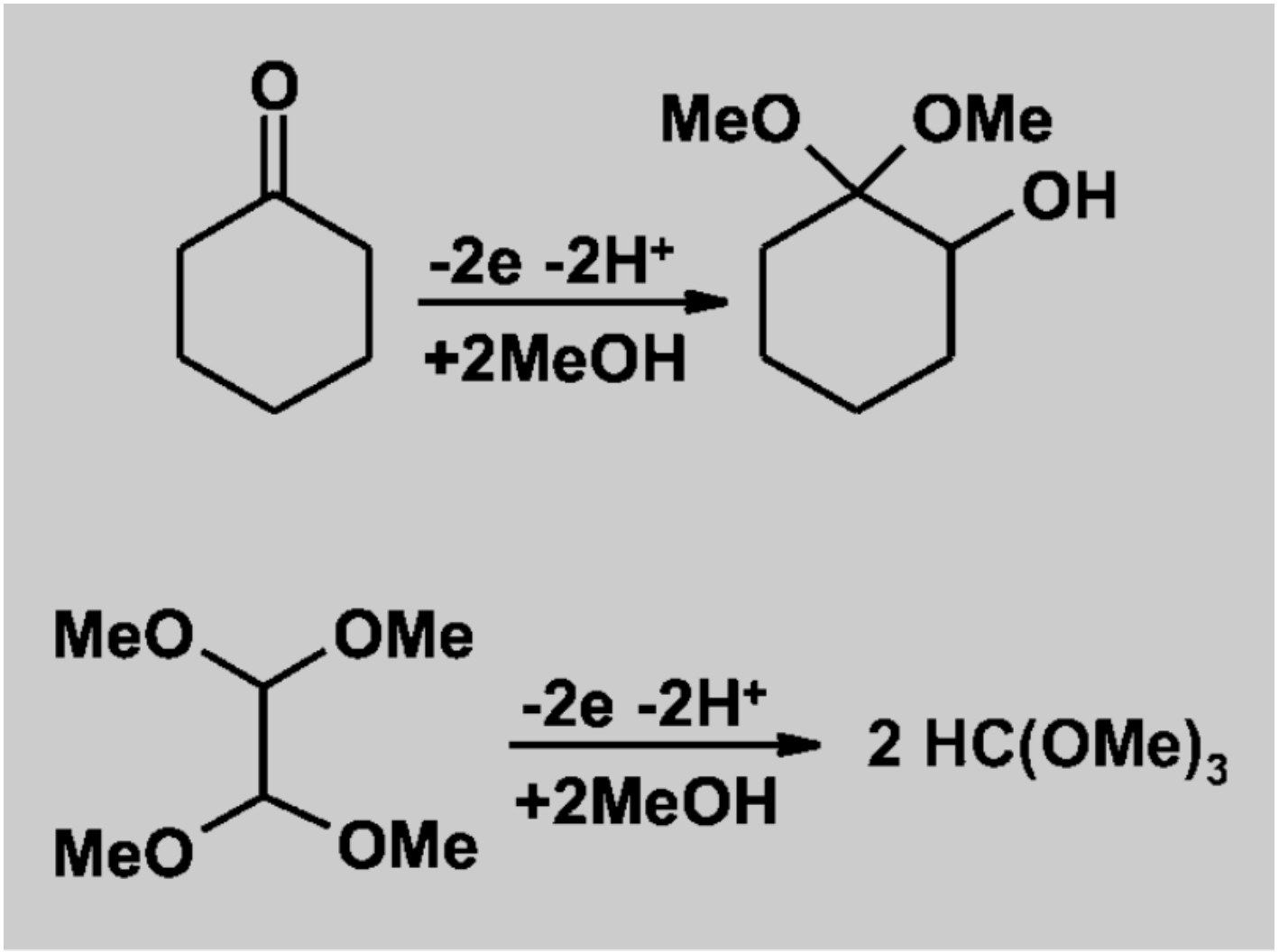
Methanol is used as solvent and reagent

Cell Voltage is 4-7V

Journal of Applied Electrochemistry (2006) 36:617–634

Electro Organic Synthesis

Same Cell/Strategy for other products: BASF



Chem. Ing. Tech. 2005, 77, 1363

Electro Organic Synthesis

Electrochemical Perfluorination

1941: J H Simons from 3M: Simons Process

- Anhy Liq HF (low temp, bp 19.5 C)
- Nickel Electrodes
- N, O, S form salts with HF and hence no electrolytes
- For hydrocarbon: KF or NaF are used as electrolytes

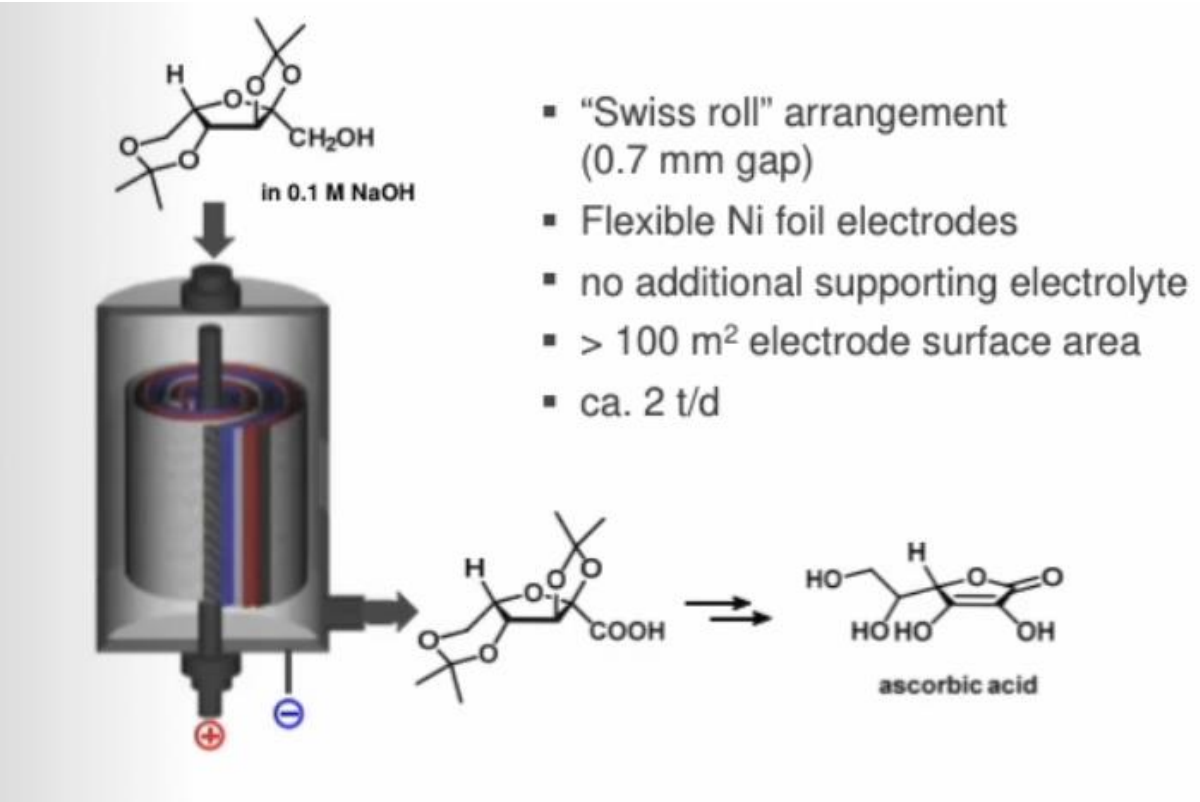
Perfluorination of Acids, Sulfonic Acids, Amines

Lubricants and Surfactants….

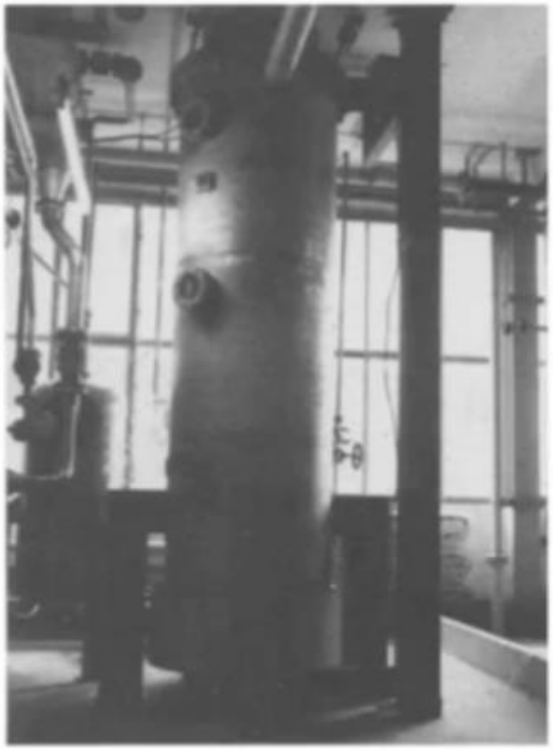
The final perfluorinated products are non-polar and their specific density is very high; therefore, they precipitate from liquid HF onto the cell bottom as a liquid

Electro Organic Synthesis

Diacetone-2-ketogulonic Acid (Vitamin C Synthesis)



- "Swiss roll" arrangement (0.7 mm gap)
- Flexible Ni foil electrodes
- no additional supporting electrolyte
- > 100 m^2 electrode surface area
- ca. 2 t/d

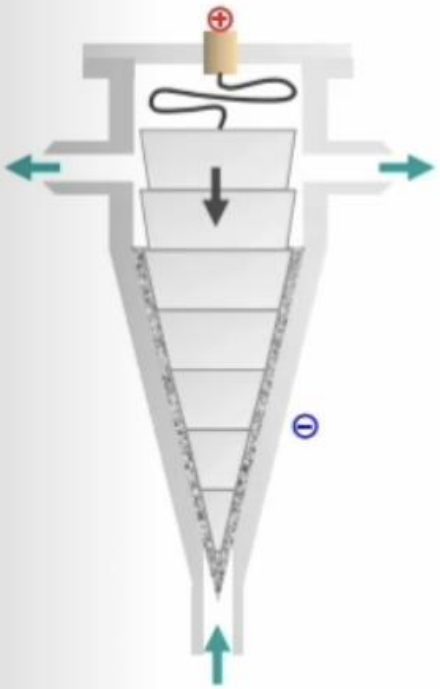


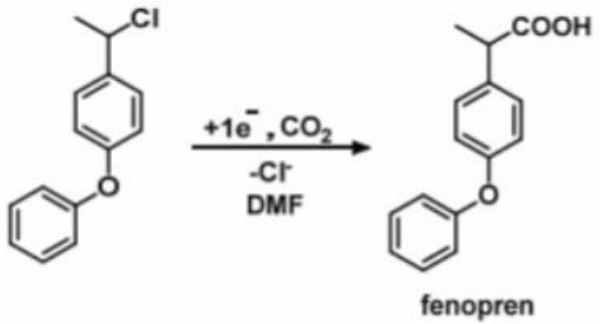
J. Electrochem. Soc. 1983, 130, 591

Electro Organic Synthesis

Scale-up of Electrosynthesis with Sacrificial Anodes

"Ingot-Eating" and "Pencil Sharpener" Reactors





fenopren

- 20 dm² cathode (steel casing)
- 3 mm PE grid interelectrode separator
- Mg anode ingot pressed down by its own weight
- Scale-up from 1 L to 30 L shown
- Up to 400 L reaction volume with a larger reactor (38 cm diameter anode rod)

Pressurized Electrolysis Plant Developed by S.N.P.E. Research Centre

SNPF France

J. Braz. Chem. Soc., Vol. 20, No. 3, 387-406, 2009.

Electro Organic Synthesis

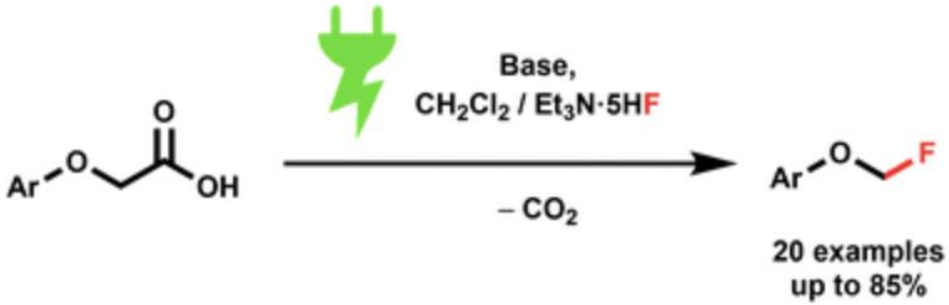
ERDC (Capenhurst) / Electrocatalytic Inc. (Gwent)

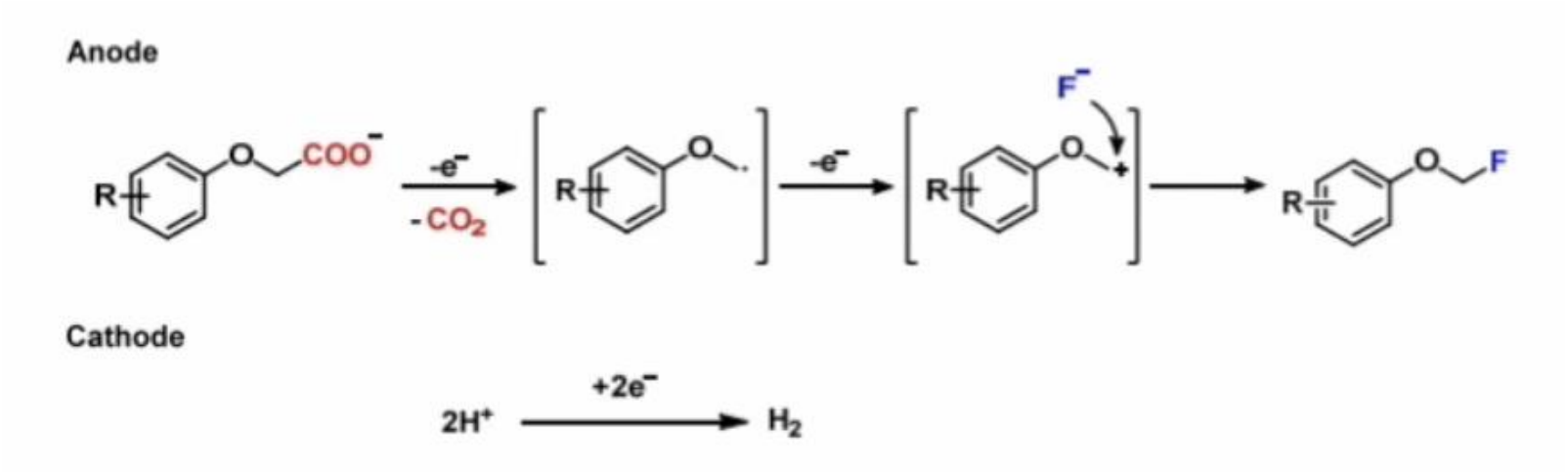
Product	Method[a]
Benzoquinone	Direct oxidation
Menadione	Indirect oxidation
Naphthoquinone	Indirect oxidation
Anisaldehyde	Indirect oxidation
p-Nitrobenzoic acid	Indirect oxidation
Dimethoxidihydrofuran	Anodic substitution
2-Methylindolene	Direct reduction
Glyoxylic acid	Direct reduction
L-Cysteine	Direct reduction
Dicarboxyphenylsulphone	Indirect oxidation - Cr(VI)
Dicarboxyphenylether	Indirect oxidation - Cr(VI)
Tolualdehyde	Indirect oxidation - Mn(III)

J. Braz. Chem. Soc., Vol. 20, No. 3, 387-406, 2009.

Electro Organic Synthesis

Sanofi-Aventis: Decarboxylative Fluorination





Chem. Sci. 2020, 11, 6053

Recent Advances in EO Chemistry

Article

Light-harvesting microelectronic devices for wireless electrosynthesis

https://doi.org/10.1038/s41586-024-08373-1

Received: 25 July 2024

Accepted: 8 November 2024

Published online: 8 January 2025

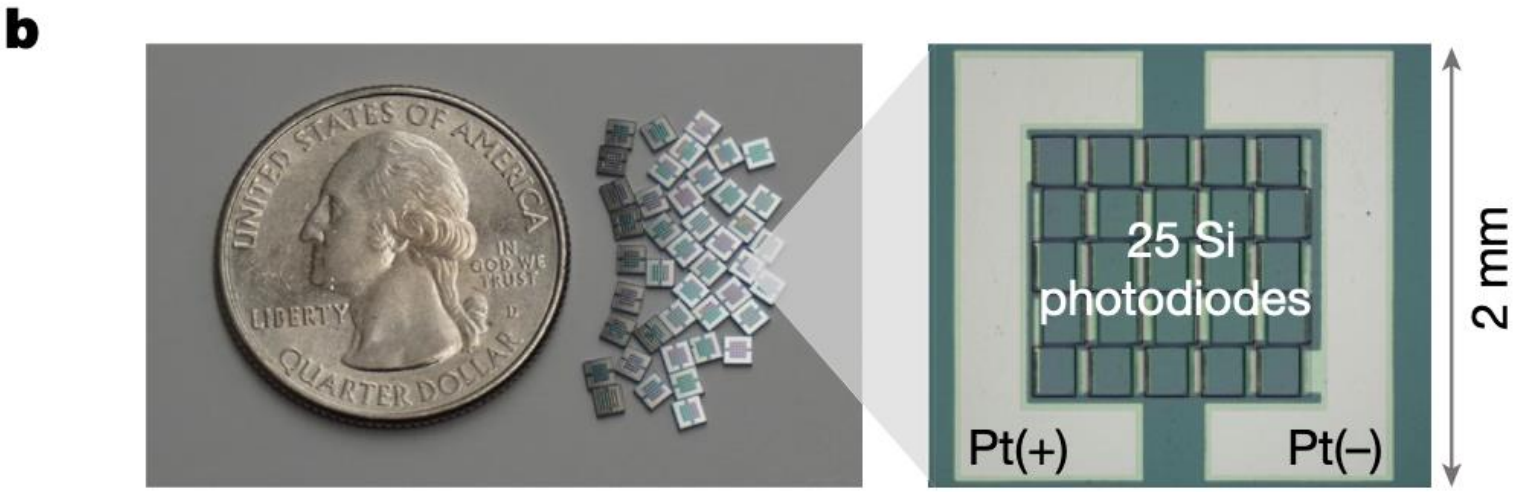
Bartosz Górski[1,4], Jonas Rein[1,4], Samantha Norris[2], Yanxin Ji[2], Paul L. McEuen[2,3]✉ & Song Lin[1,3]✉

High-throughput experimentation (HTE) has accelerated academic and industrial chemical research in reaction development and drug discovery and has been broadly

SPECS:

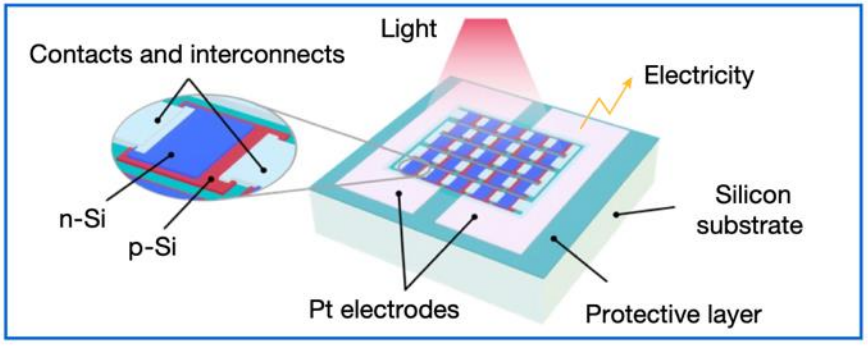
Small Photoelectronics for Electrochemical Synthesis

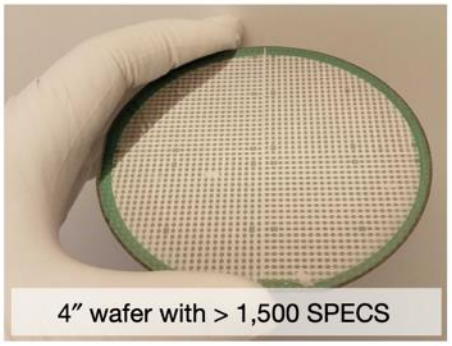
Recent Advances in EO Chemistry

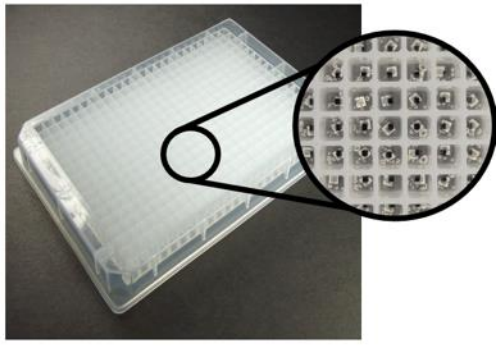


Features of SPECS:

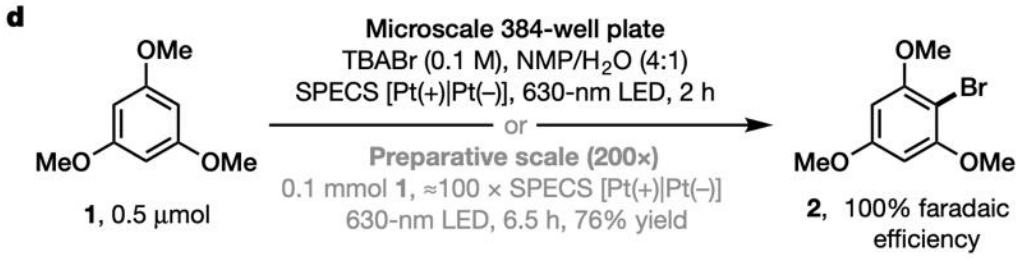
- ❑ 384 parallel experiments
- ❑ Wireless and easy to operate
- ❑ Open-circuit voltage ≈ 12 V
- ❑ Variable electrode materials
- ❑ Chemically resistant and reusable
- ❑ Microscale synthesis (≈20 µl)

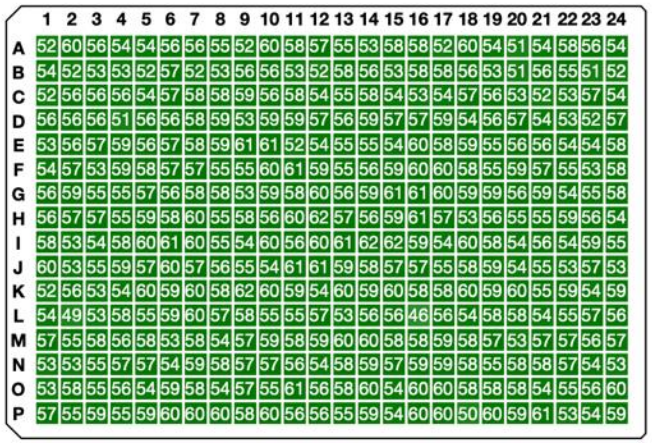




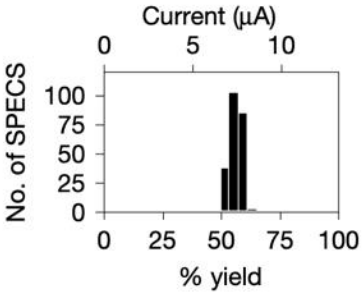


Recent Advances in EO Chemistry





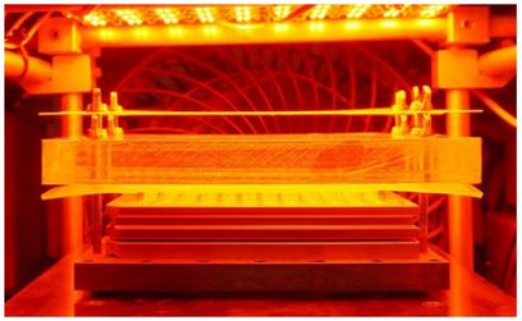
Yield ∝ time × current
Yield = 57 ± 3%
Current = 7.6 ± 0.3 µA



96-well or 384-well plate

LED array

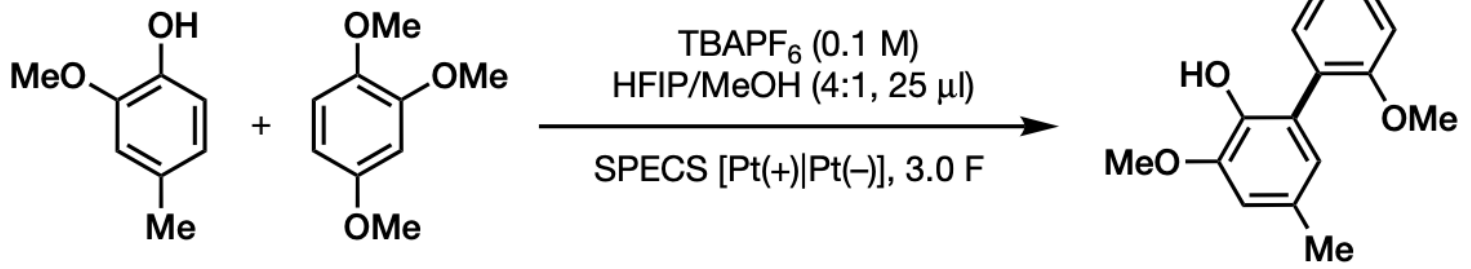
+ SPECS



Recent Advances in EO Chemistry

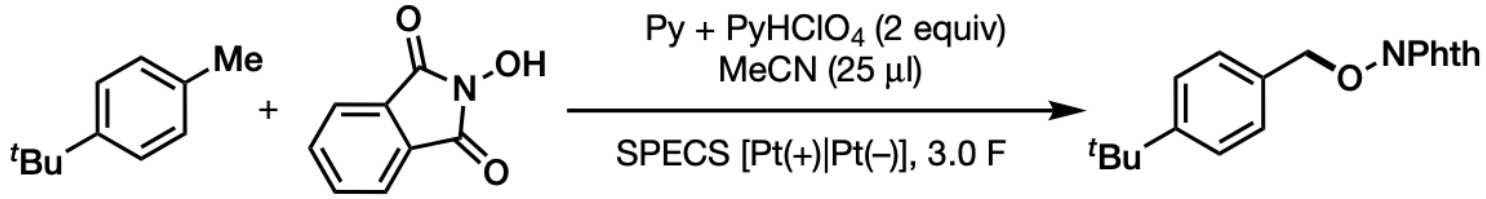
a

❒ Direct electrolysis:



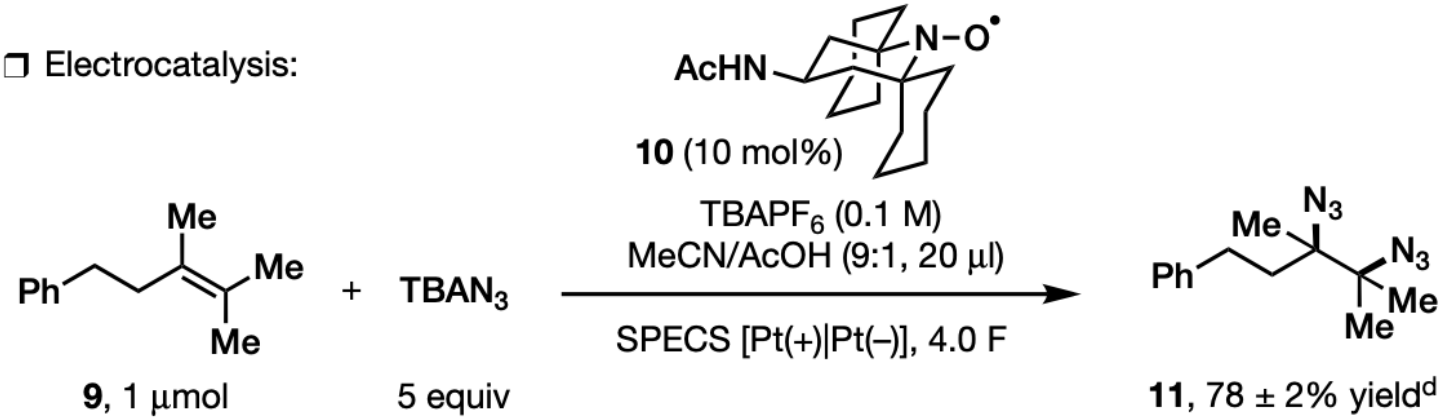
3, 1 µmol **4**, 3 equiv **5**, 64 ± 2% yield[a]

❒ Mediated electrolysis:



6, 2 equiv **7**, 1 µmol **8**, 53 ± 2% yield[b,c]

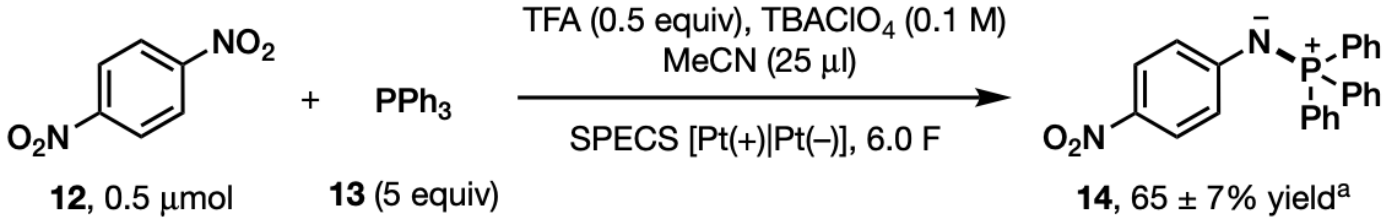
❒ Electrocatalysis:



9, 1 µmol 5 equiv **11**, 78 ± 2% yield[d]

❒ Convergent paired electrolysis:

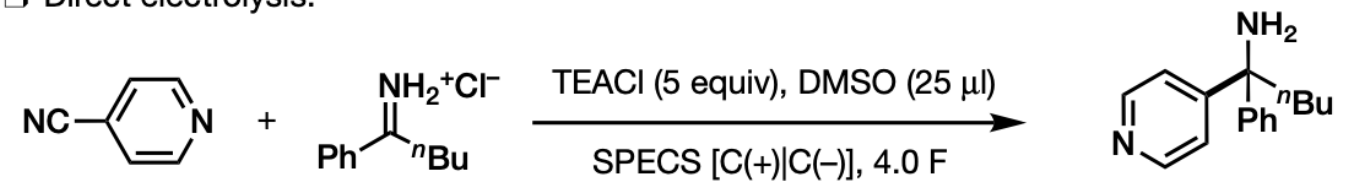
Recent Advances in EO Chemistry



12, 0.5 µmol + **13** (5 equiv) → **14**, 65 ± 7% yield[a]

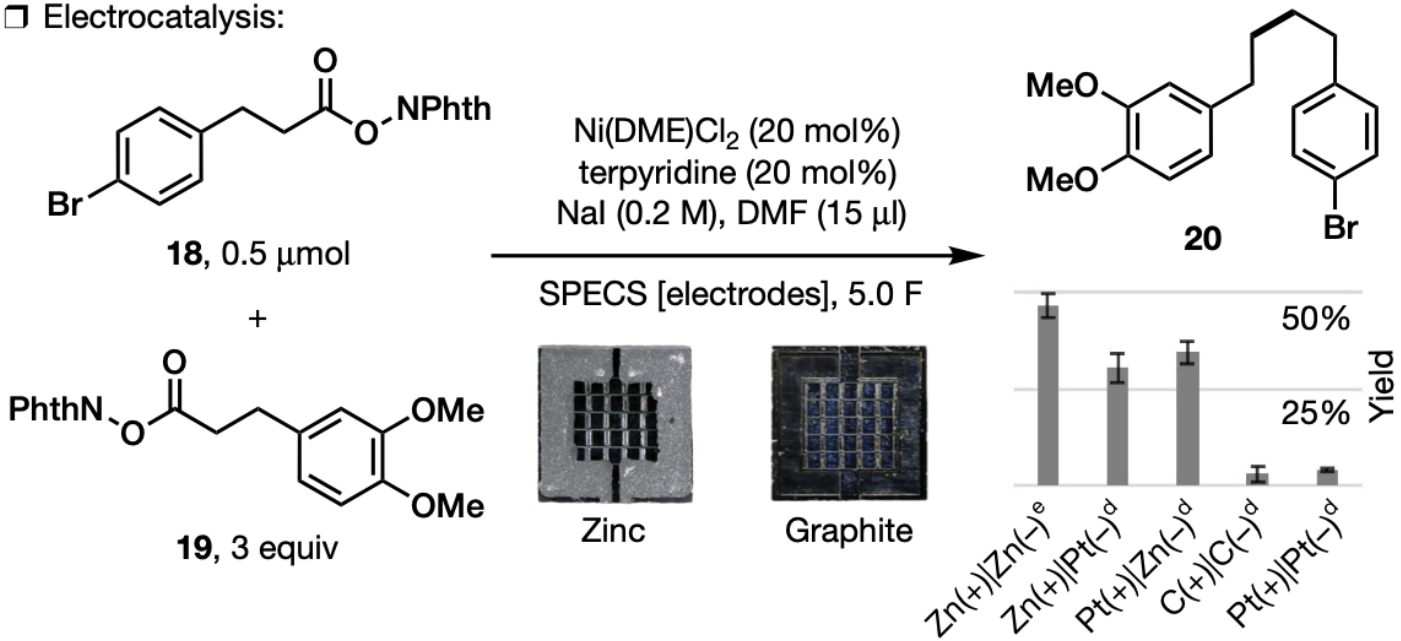
b

❒ Direct electrolysis:



15, 1 µmol + **16**, 2.2 equiv → **17**, 41 ± 4% yield[a]

❒ Electrocatalysis:



18, 0.5 µmol + **19**, 3 equiv

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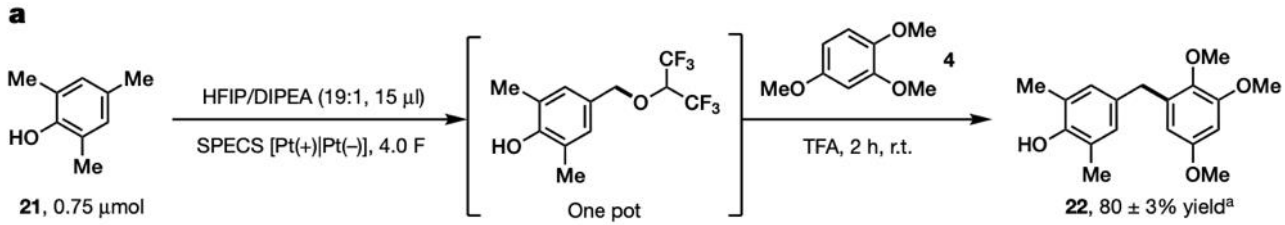
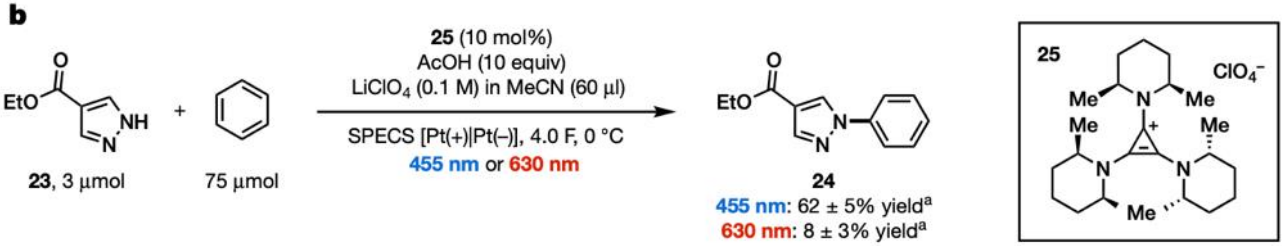
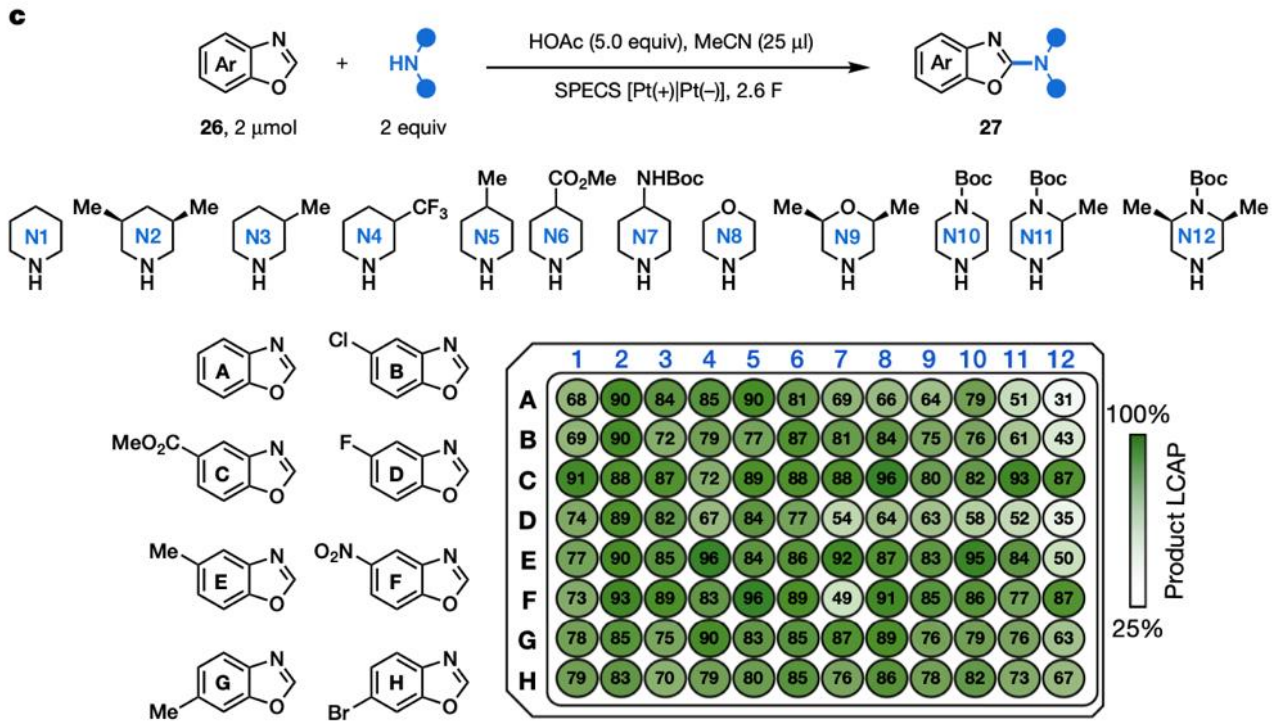
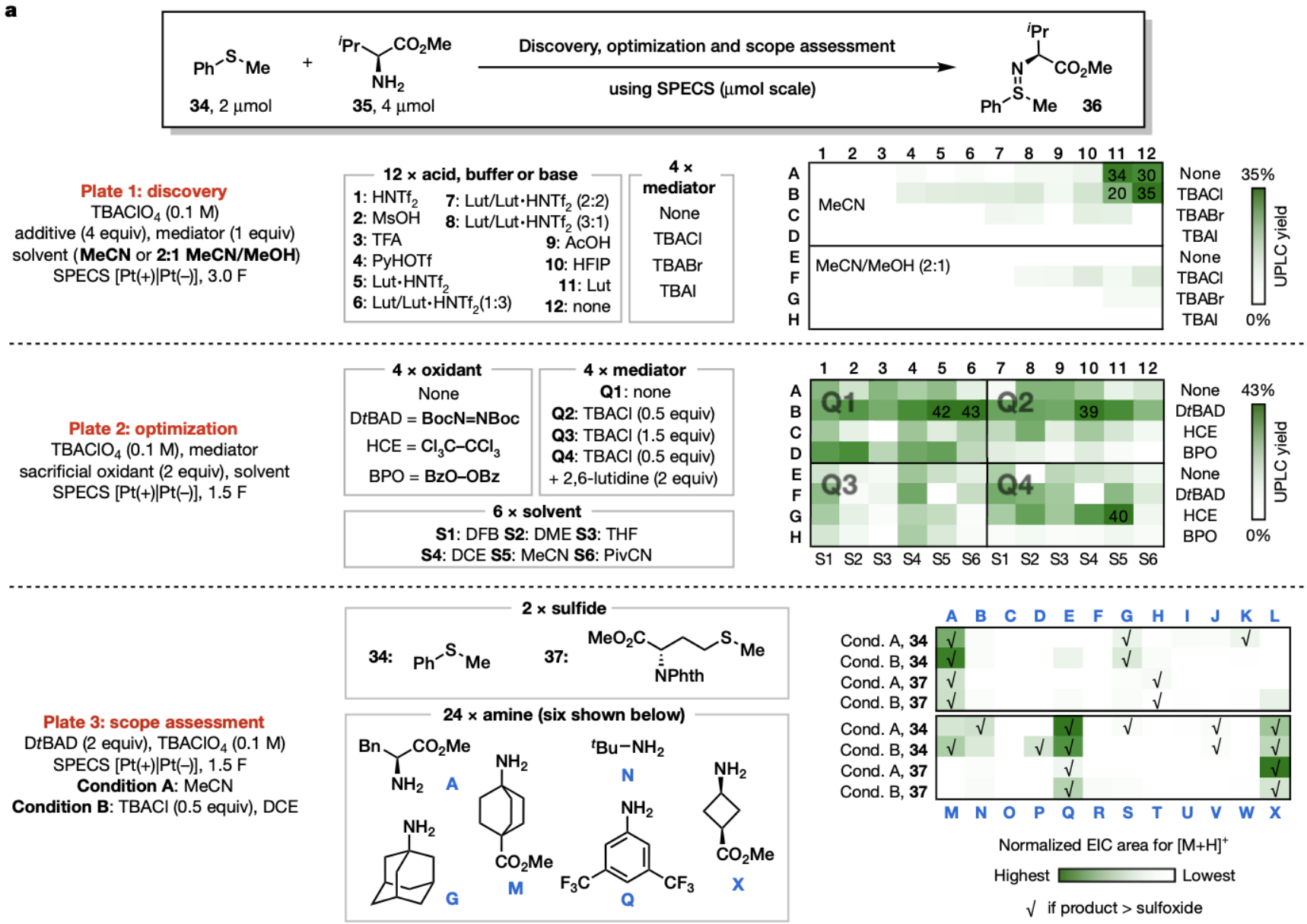




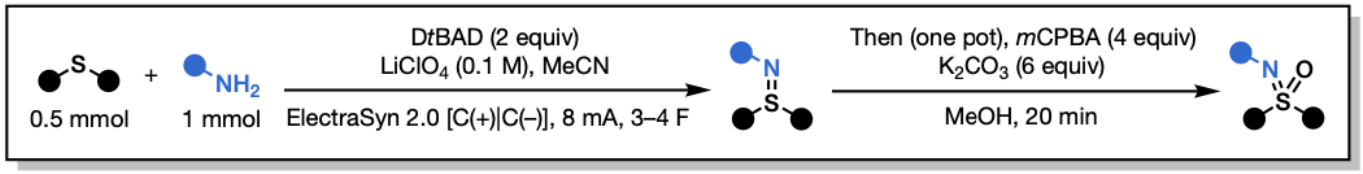


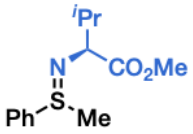
Recent Advances in EO Chemistry



Recent Advances in EO Chemistry

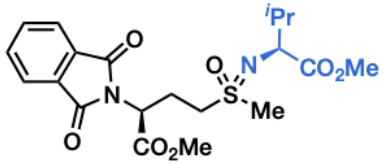
b



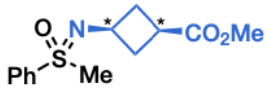


36, 54% yield, 1:1.4 dr
(88% yield, 1:1.2 dr)[a]
(72 ± 3% yield with SPECS)[b]

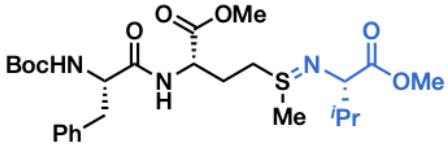
38, 78% yield, 1:1.2 dr
over two steps



39, 68% yield, 1:1.2 dr
over two steps



40, 32% yield, 10:1 dr
(with respect to *carbons)
over two steps



41, 83% yield[c], 1:1.1 dr

Recent Advances in EO Chemistry

ORGANIC PROCESS RESEARCH & DEVELOPMENT
OPR&D

pubs.acs.org/OPRD

Article

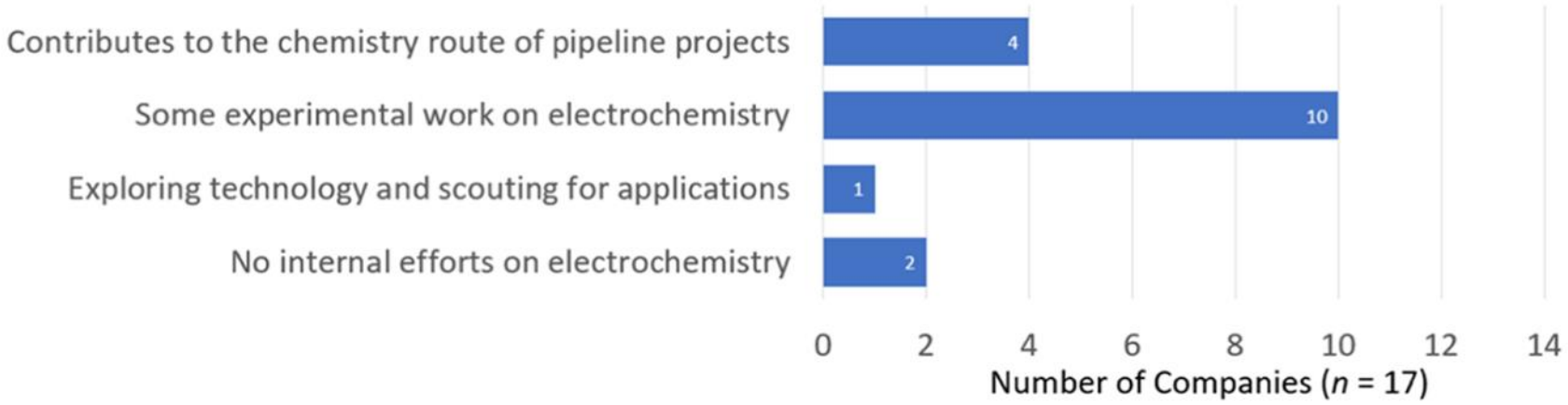
Adoption of Electrochemistry within the Pharmaceutical Industry: Insights from an Industry-Wide Survey

Antonio C. Ferretti,* Benjamin Cohen, Lin Deng, Moiz Diwan, Michael O. Frederick, and Dan Lehnherr

Cite This: *Org. Process Res. Dev.* 2025, 29, 322–332

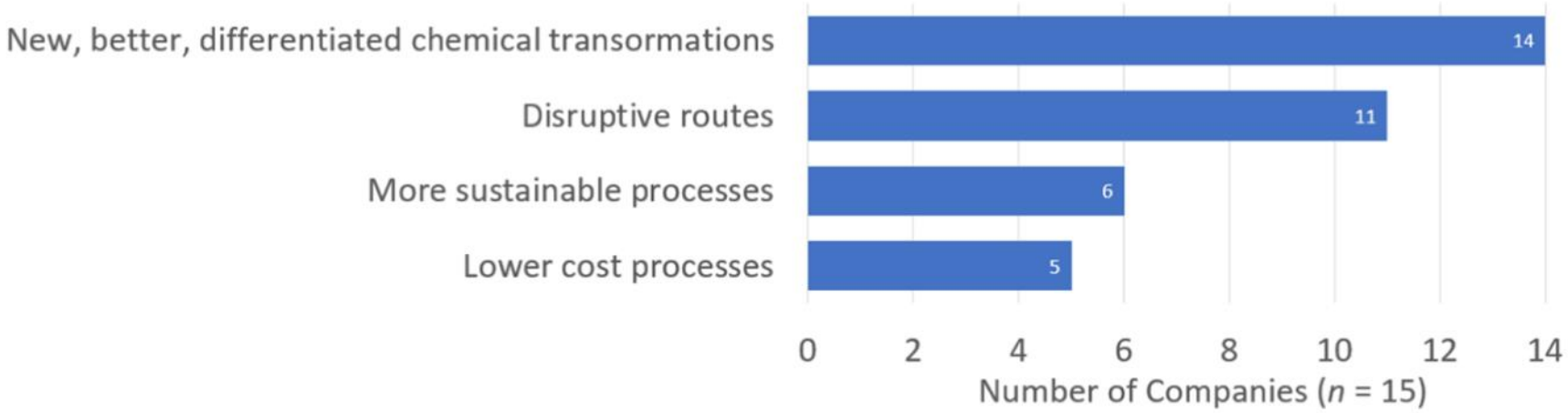
Read Online

To what extent is your company using electrochemistry? *[Select all that apply]*

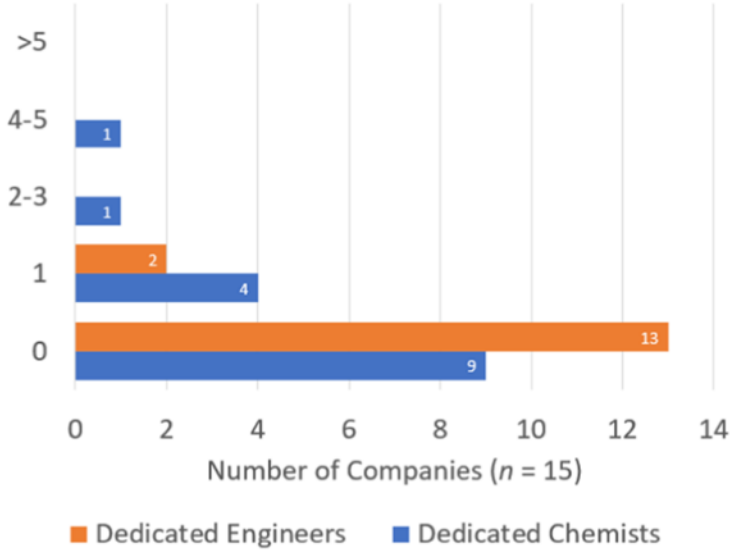


Recent Advances in EO Chemistry

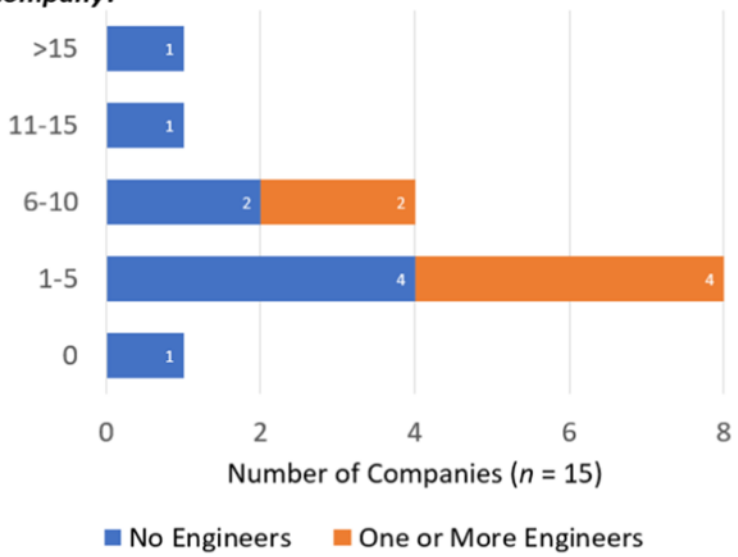
Why did your company start being involved in organic electrochemistry? *[Select all that apply]*



How many people spend more than 50% of time on electrochemistry in your company?

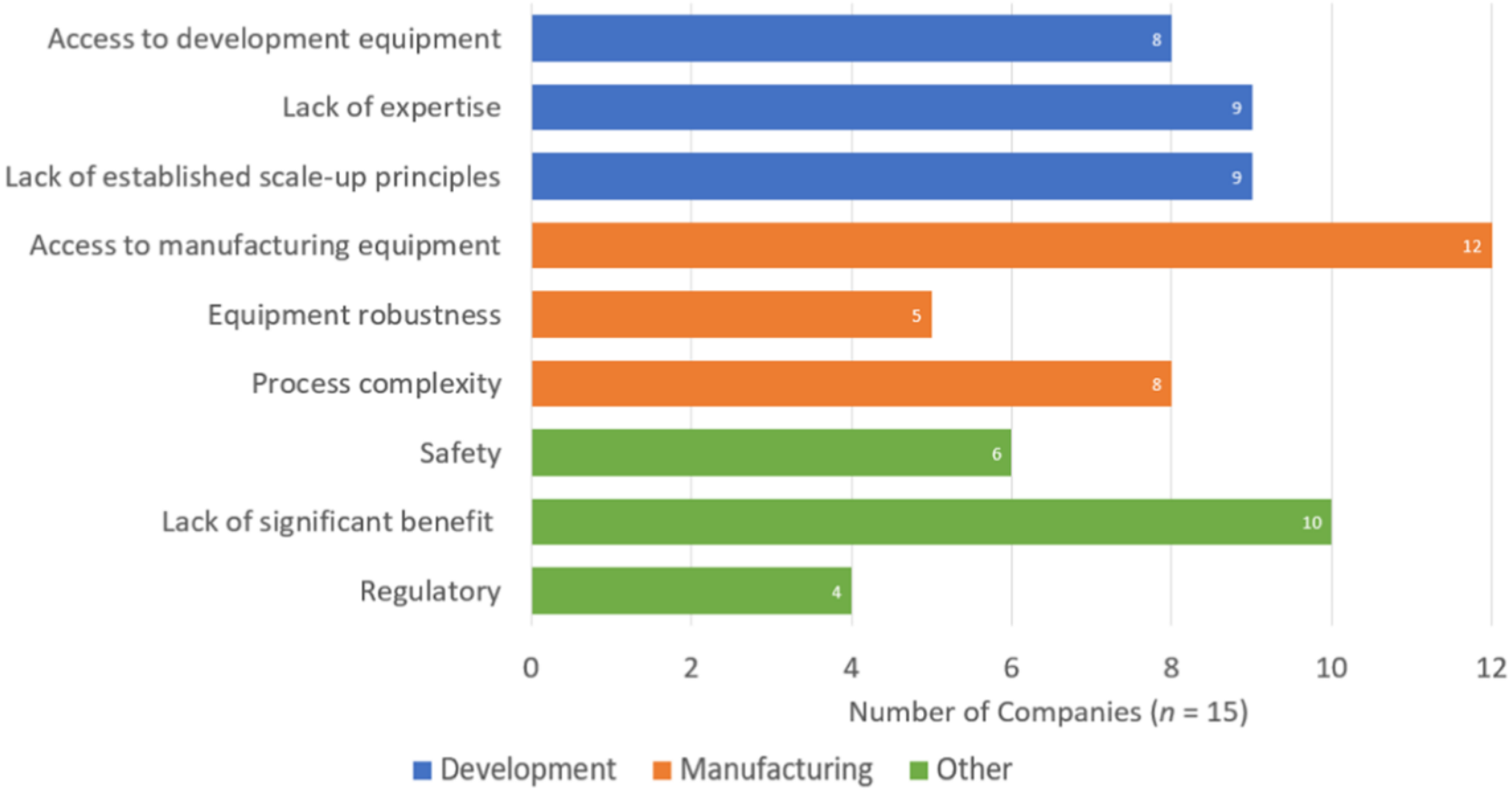


How many chemists do you estimate have performed some laboratory work on electrochemistry overall while at your company?



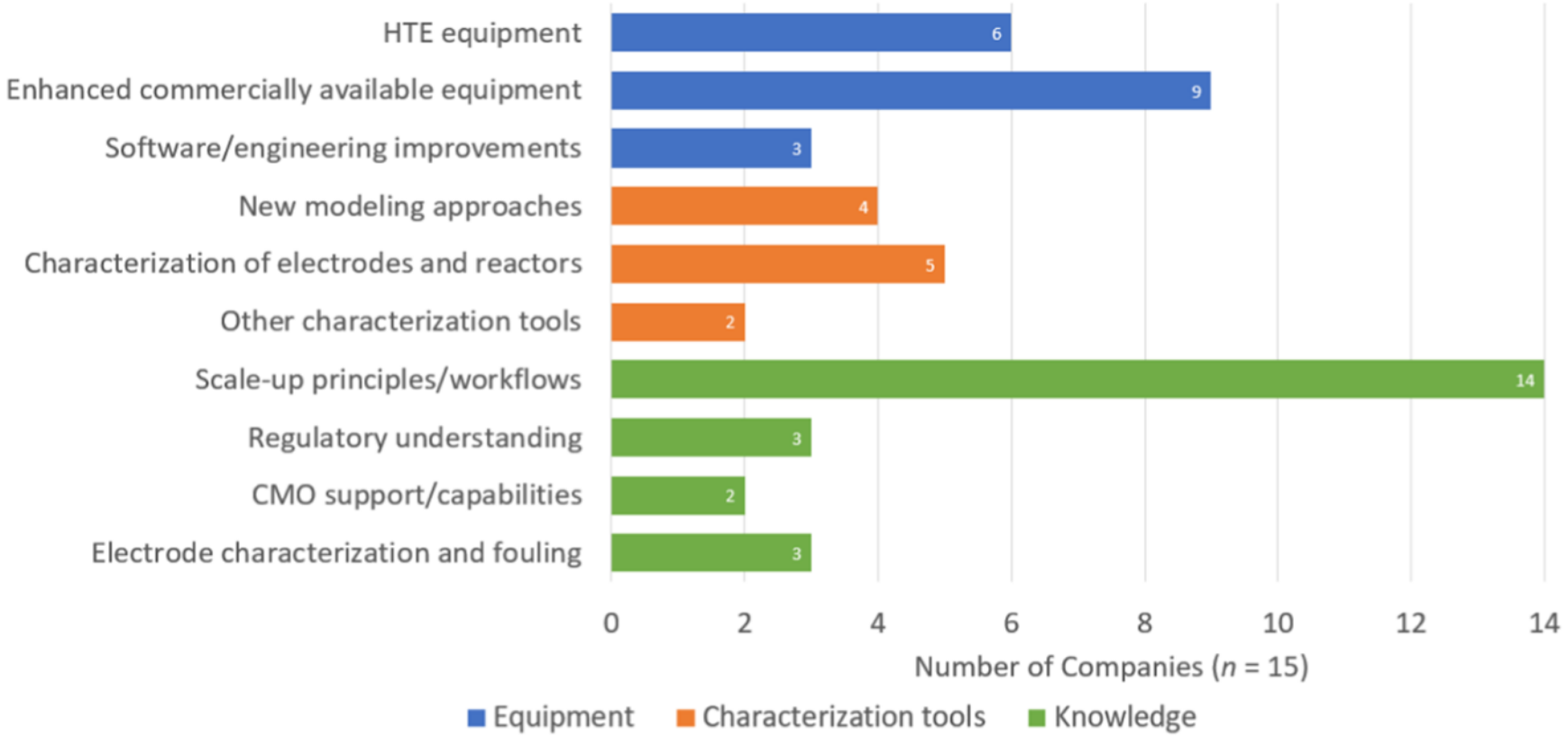
Recent Advances in EO Chemistry

What are the roadblocks for the development and adoption of electrochemical processes in a commercial setting? *[Select all that apply]*



Recent Advances in EO Chemistry

What development equipment, manufacturing equipment, tools to characterize electrochemical reactors, knowledge, currently not available, are needed? *[List up to 3 in order of potential impact, open question]*



Continuous Process Intensification

Electro Organic Chemistry

Future is bright

Journey has just started

There is a long road ahead