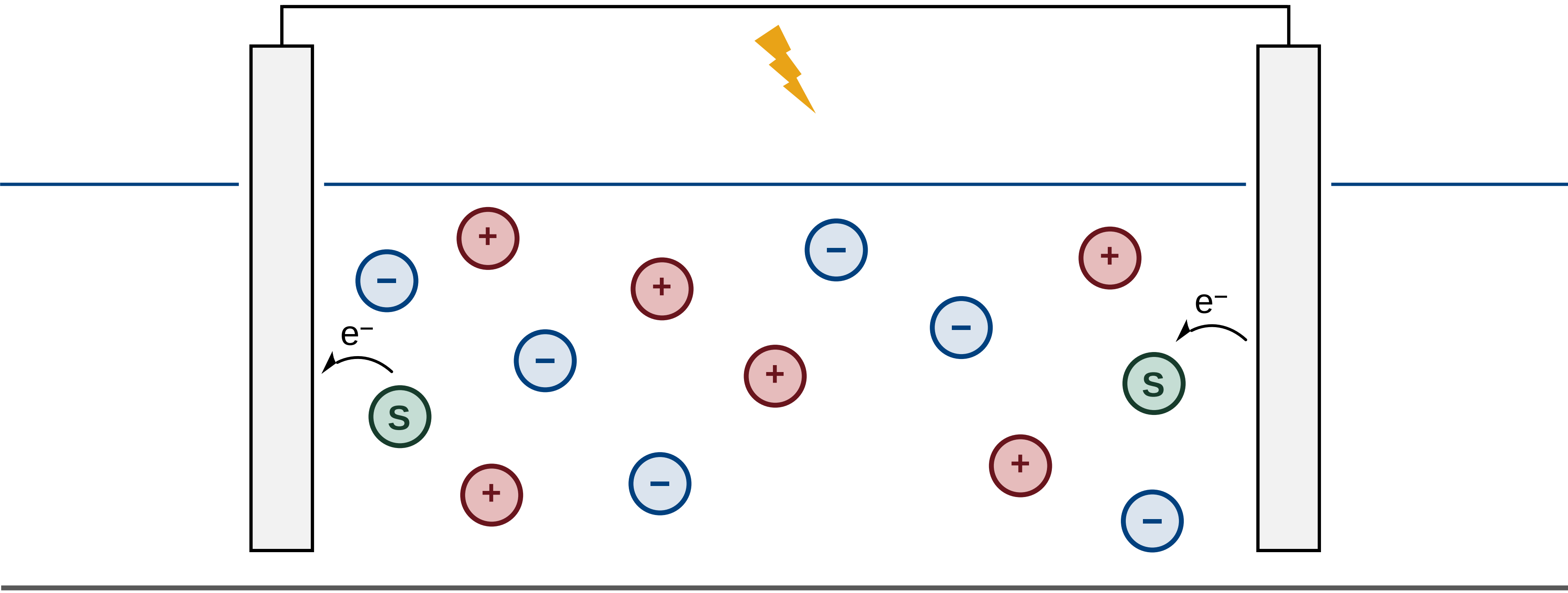
Electrocatalysis

Literature Review

28 February 2023

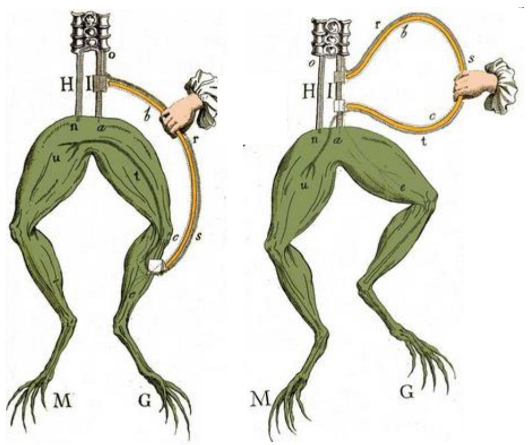
Colin A. Gould

What is electrochemistry?



electrochemistry is the study of chemical reactions that occur through the application of an electrical potential

History of electrochemistry

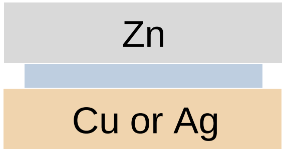


frog's leg twitches when it forms a circuit between two metals

-Luigi Galvani (1786)

"animal electricity"

"Volta pile" was the first electrical battery



electrical current formed when copper and zinc are connected by brine-soaked cloth

-Alessandro Volta (1800)

electricity comes from two metals interacting through electrolyte

Volta pile (1800)

"The Voltaic Pile," libraries.mit.edu

History of electrochemistry

Volta pile

$$2\,H_2O \longrightarrow 2\,H_2 + O_2$$

first electrolysis of water with a constant electrical supply (first electrochemical reaction)

-Nicholson and Carlisle (1800)

Na, K, Ca, B, Ba, Sr, Mg

discovery and isolation of seven new elements by electrolysis of molten salts

-Humphry Davies (1807-1808)

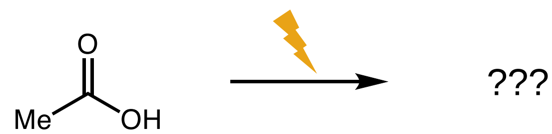
electrolysis (1800)

Volta pile (1800)

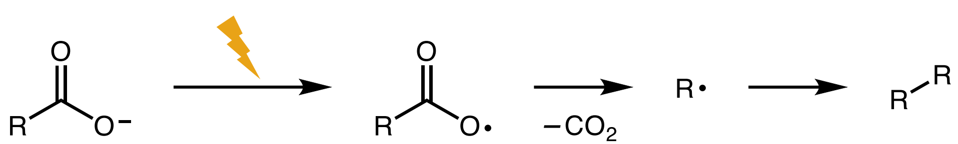
Voltaic pile," Wikipedia

History of electrochemistry

early examples of organic electrochemistry:



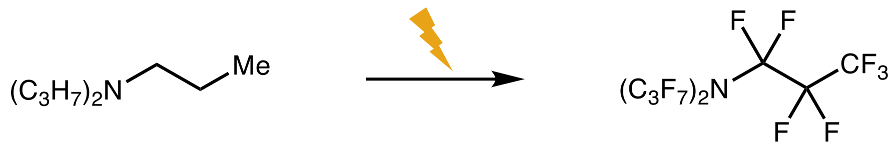
-Michael Faraday (1834)



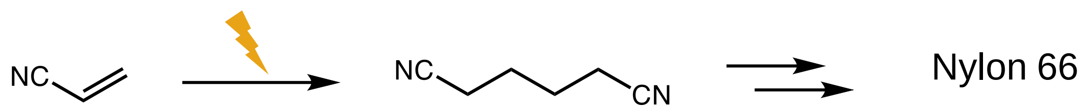
-Hermann Kolbe (1847)

History of electrochemistry

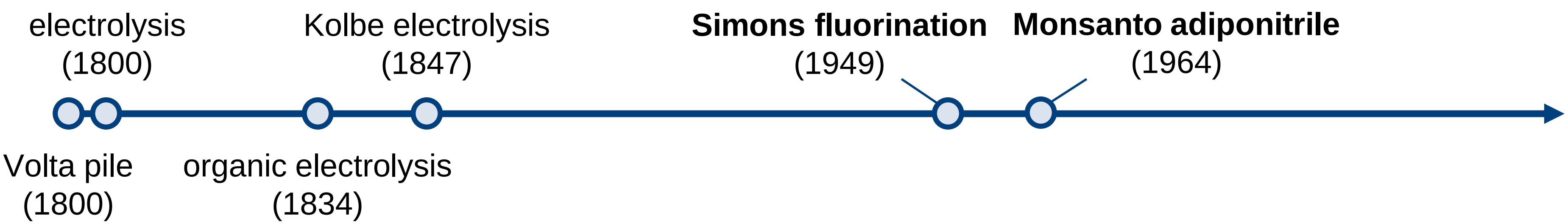
early applications of electrochemistry to industry:



-Simons fluorination (1949)

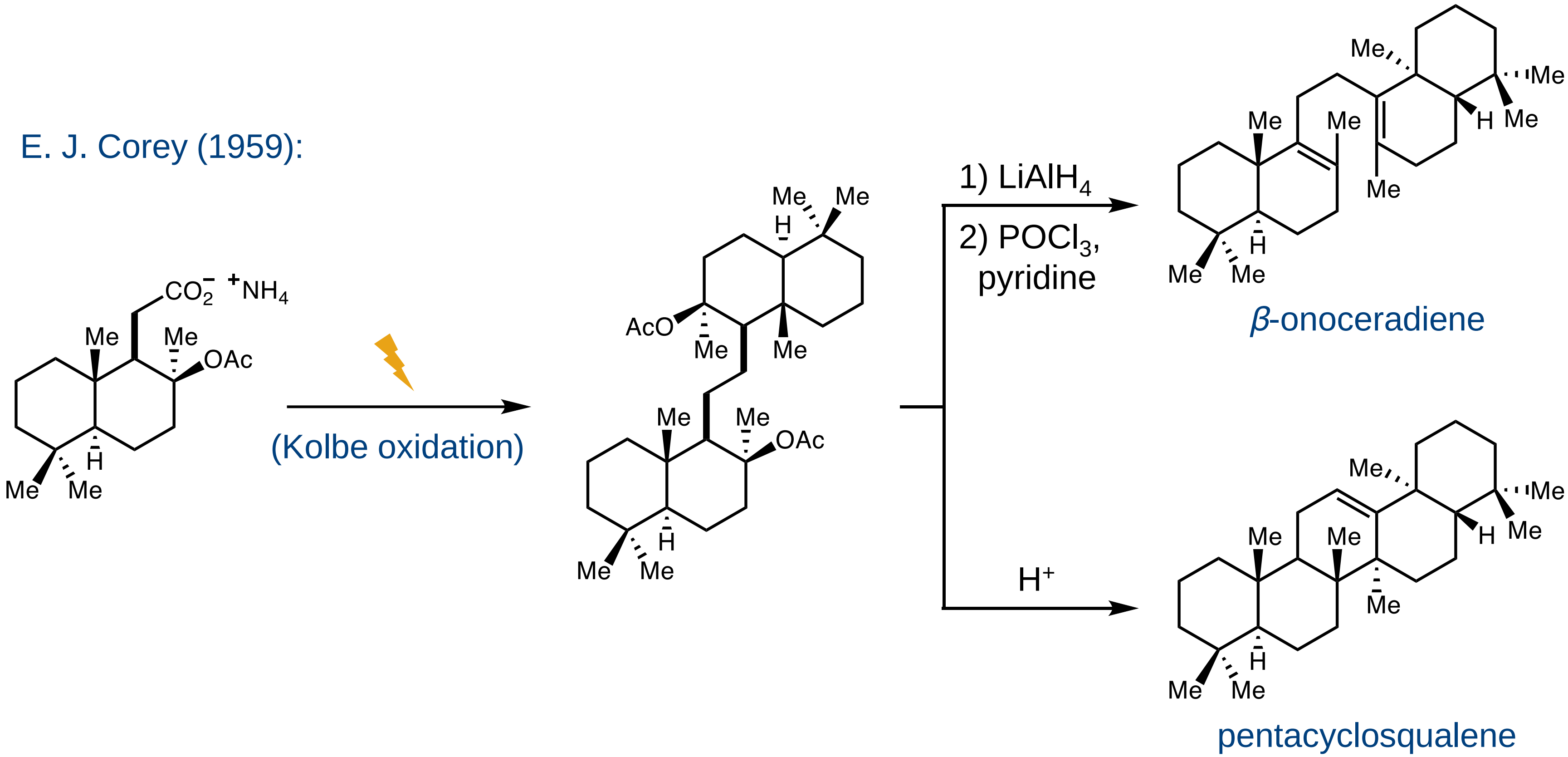


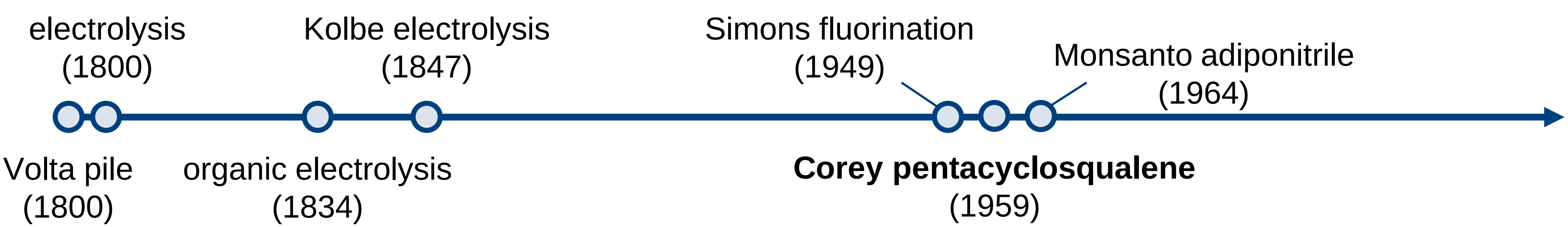
-Monsanto adiponitrile process (1964)



History of electrochemistry

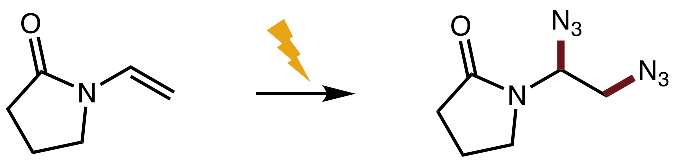
E. J. Corey (1959):



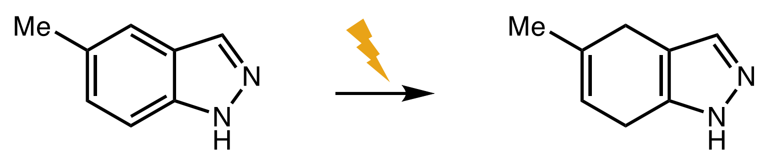


Corey, E. J.; Sauers, R. R. J. Am. Chem. Soc. **1958**, 81, 1739

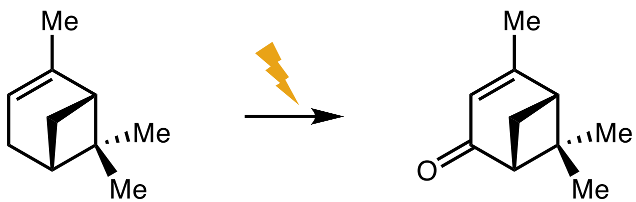
History of electrochemistry



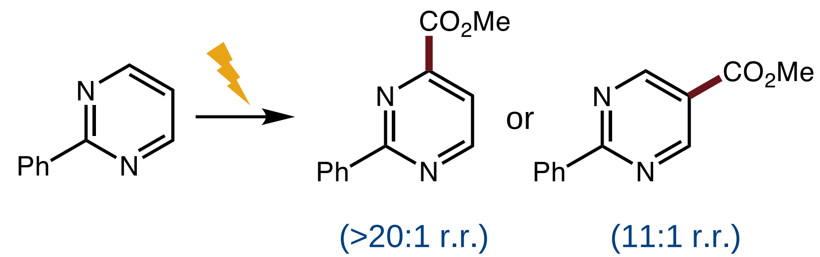
Lin, S.; et. al. Science **2017**, 357, 575



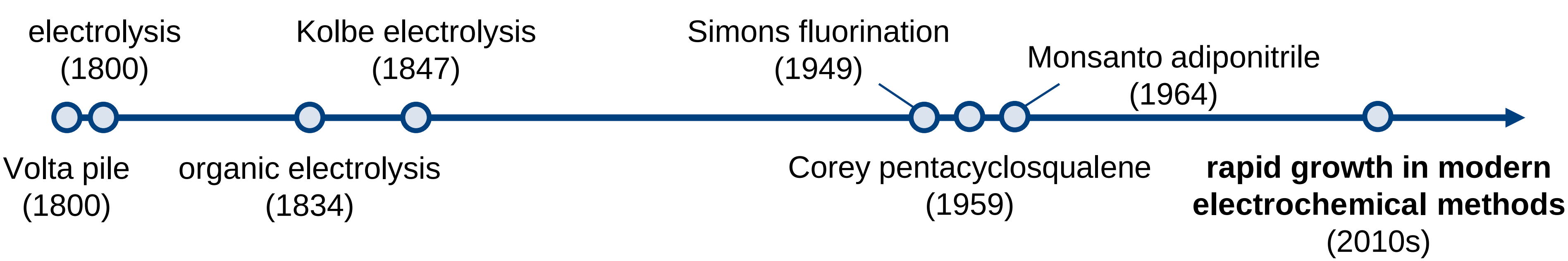
Baran, P. S.; et. al. Science **2019**, 363, 838



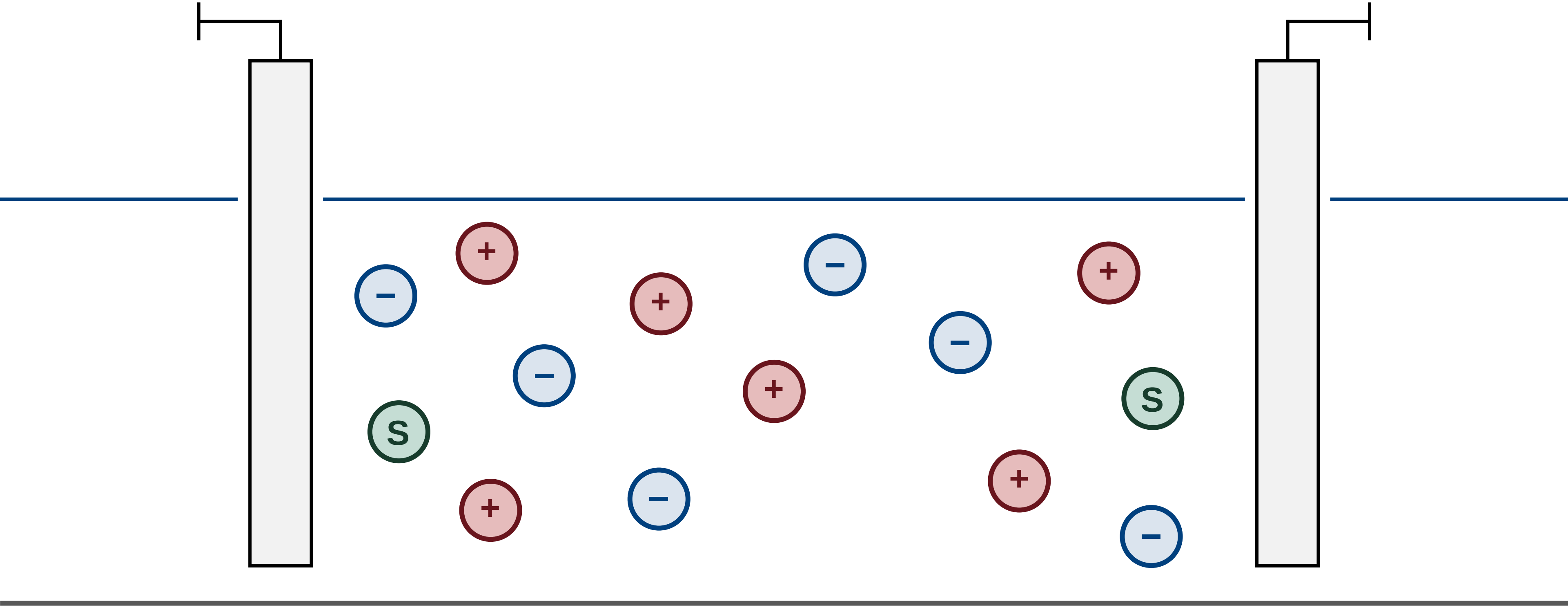
Baran, P. S.; et. al. Nature **2016**, 533, 77



Lin, S.; et. al. Nature **2023**



Electrocatalysis Part 1: A Practical Guide to EChem

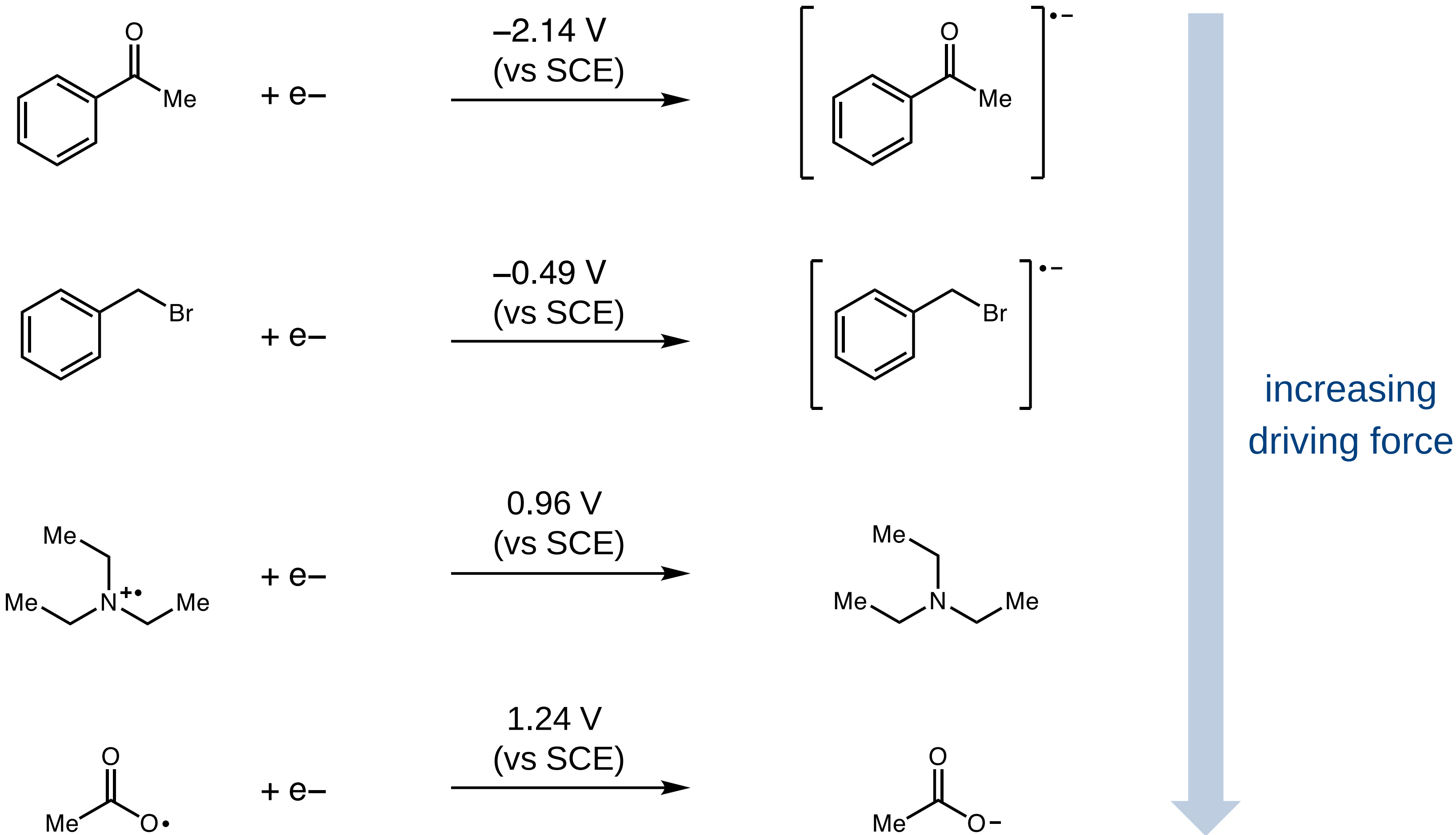


some helpful tutorials:

Schotten, C.; Willans, C. E.; et. al. Green Chem. **2020**, 22, 3358

Kingston, C.; Baran, P. S.; et. al. J. Am. Chem. Soc. **2019**, 53, 72

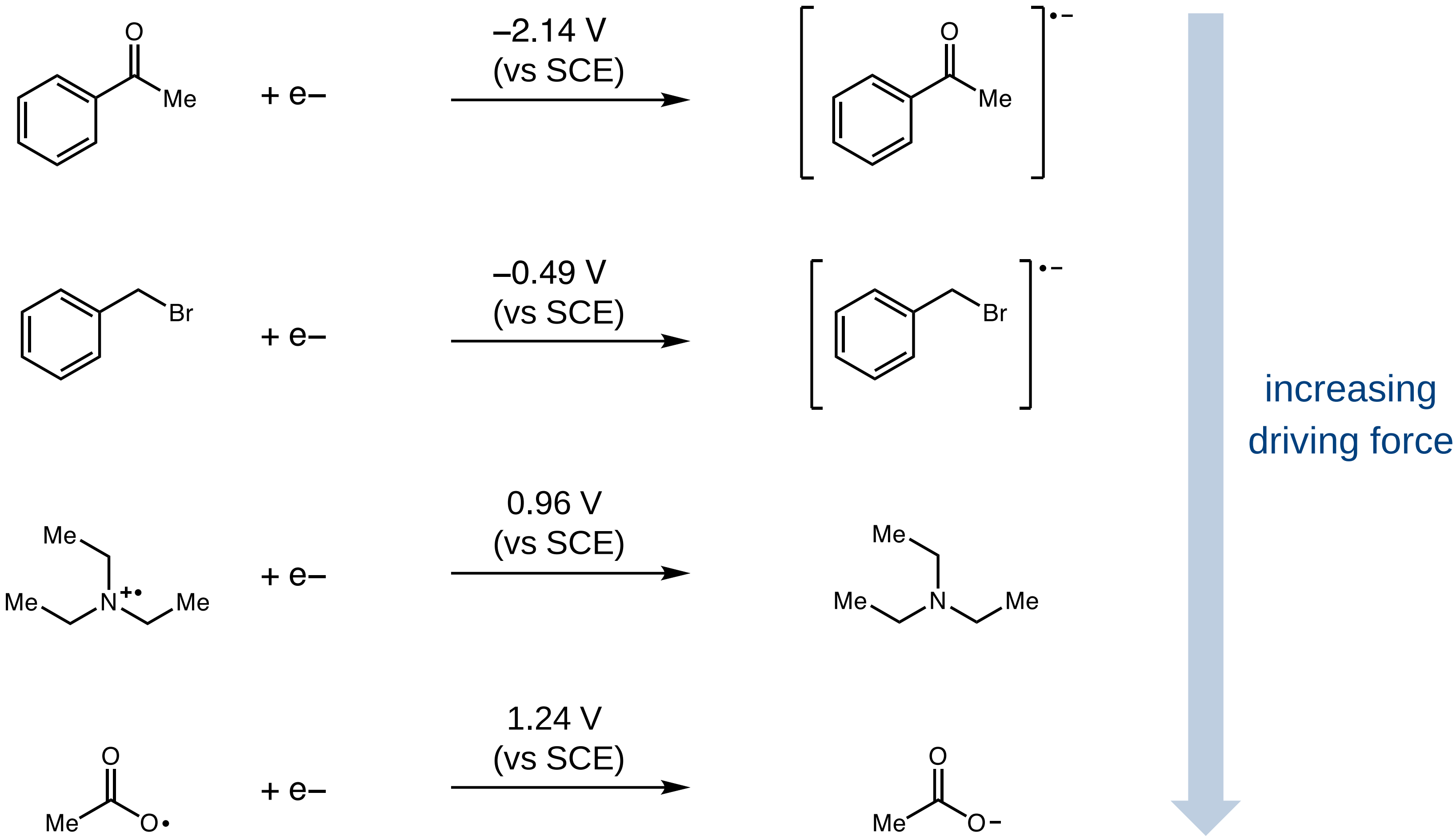
Reduction potentials of organic molecules



formalism is to report the potential of reduction half-reactions

macmillan.princeton.edu, “Merck Photocatalysis Chart”

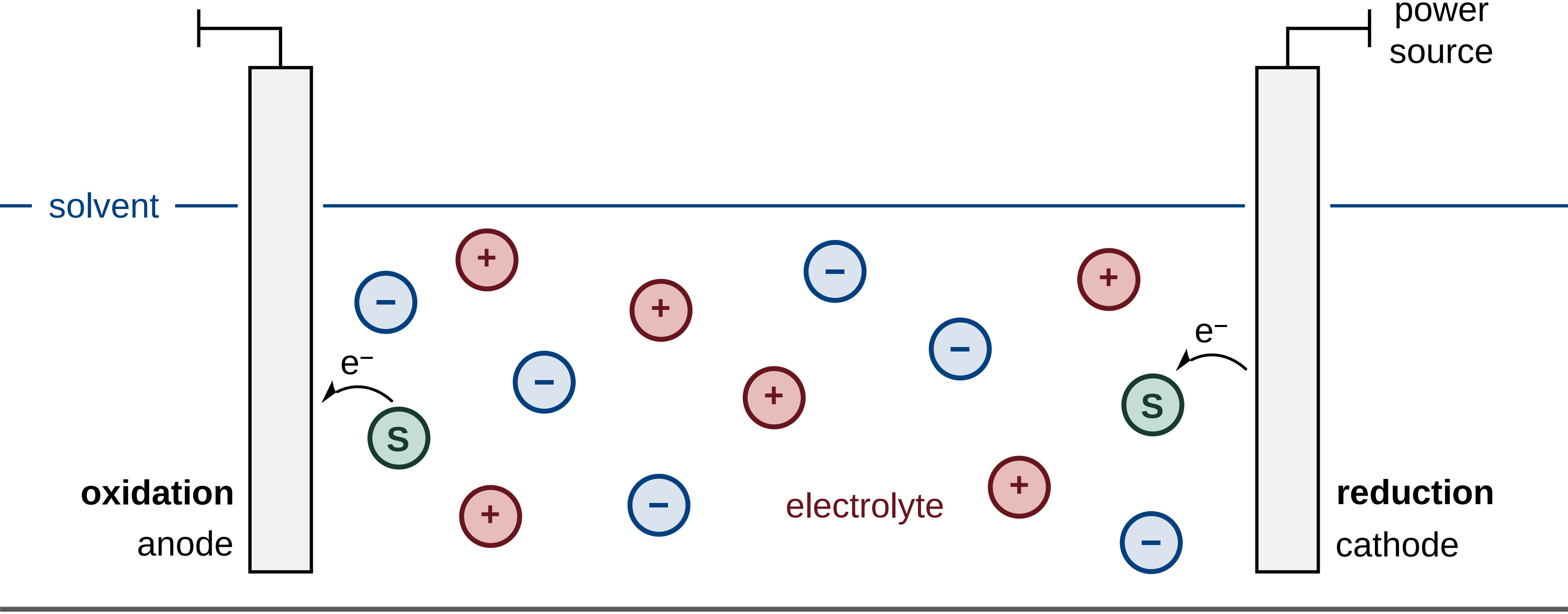
Reduction potentials of organic molecules



important to measure potentials via **cyclic voltammetry** (CV)
when designing an electrocatalytic reaction

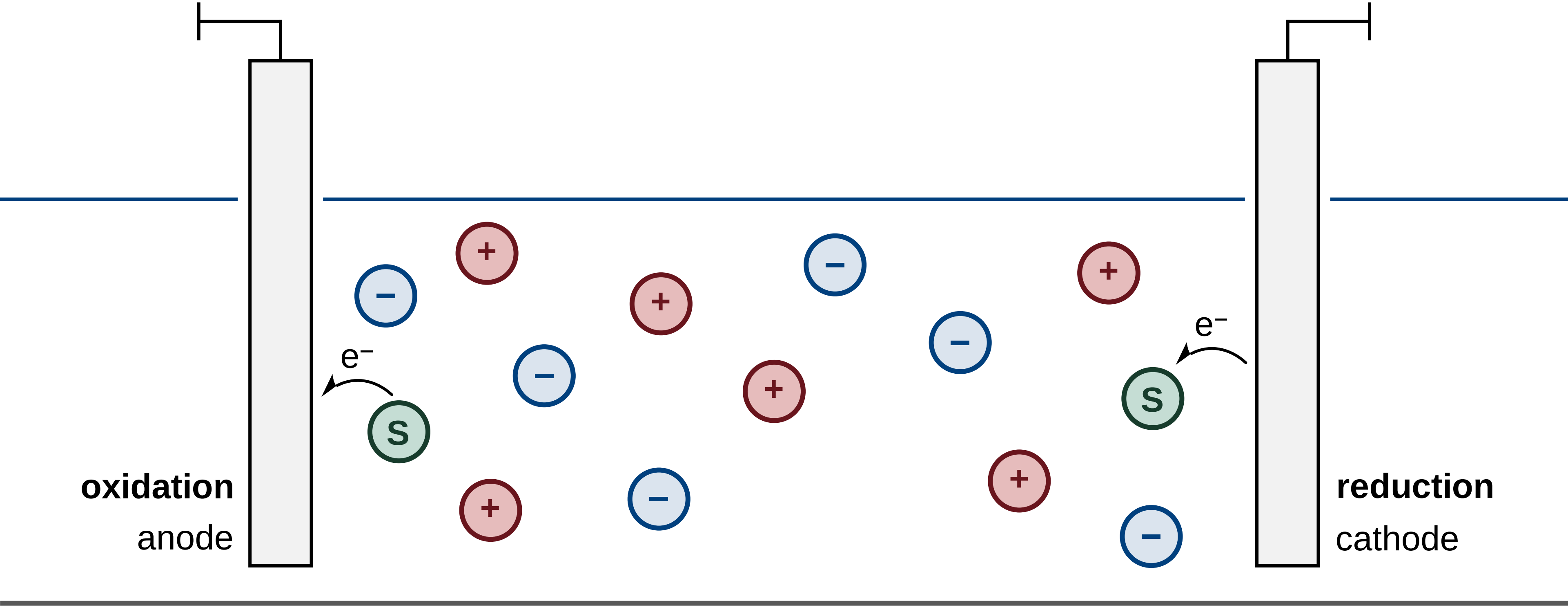
macmillan.princeton.edu, “Merck Photocatalysis Chart”

Components of an electrochemical cell



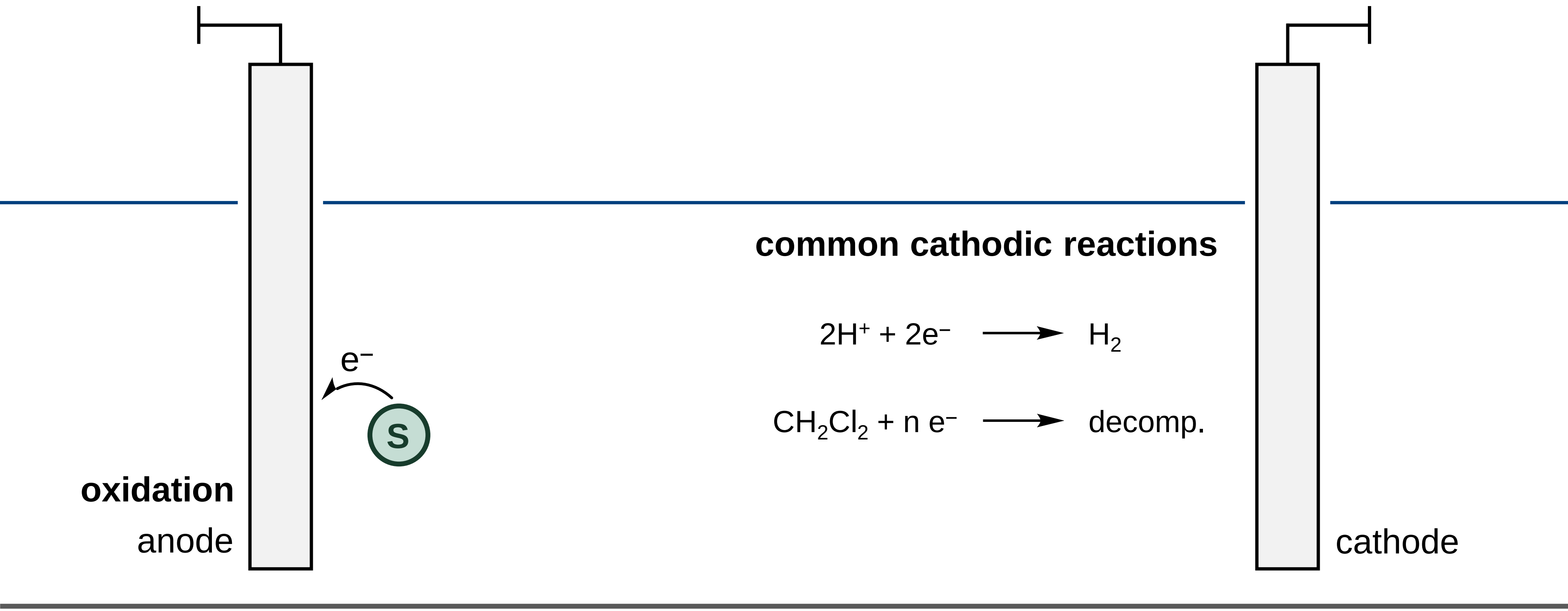
oxidation occurs at the anode and reduction
occurs at the cathode

Designing an electrochemical cell



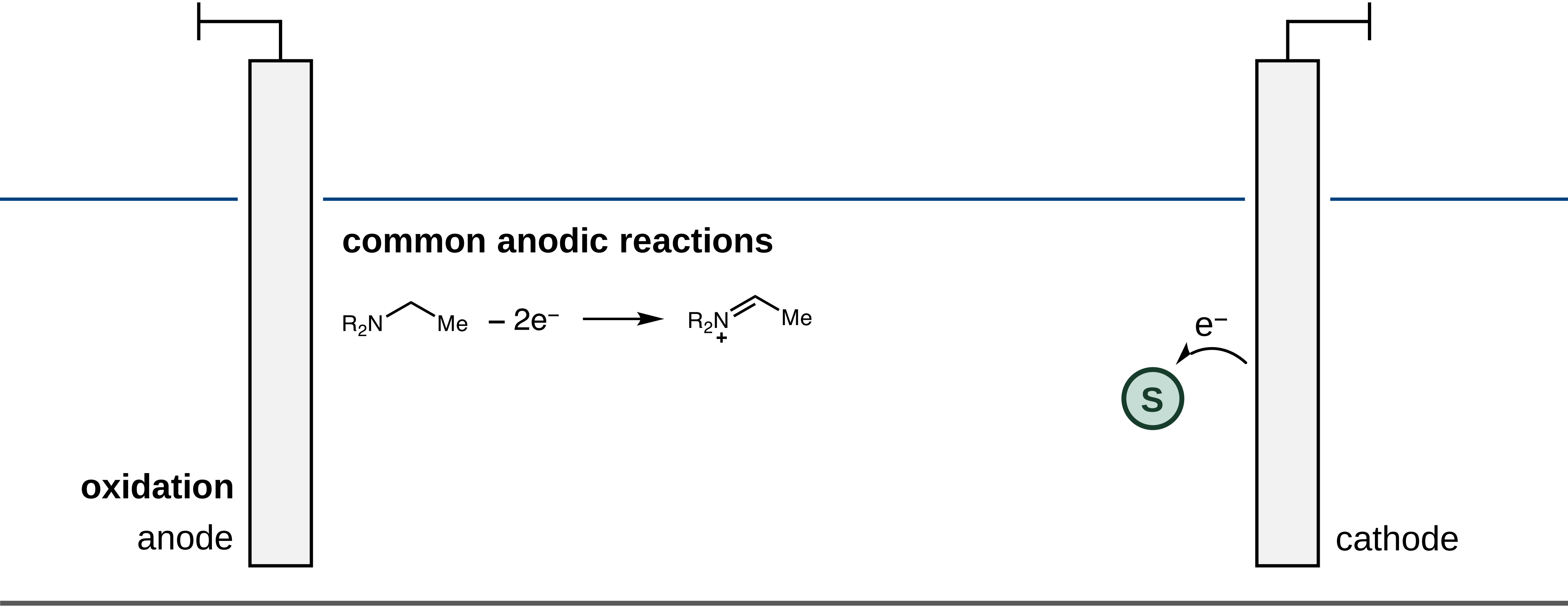
Electrochemical cells must be balanced, so for every electron removed from a substrate at the anode, an electron is added to a substrate at the cathode

Designing an electrochemical cell



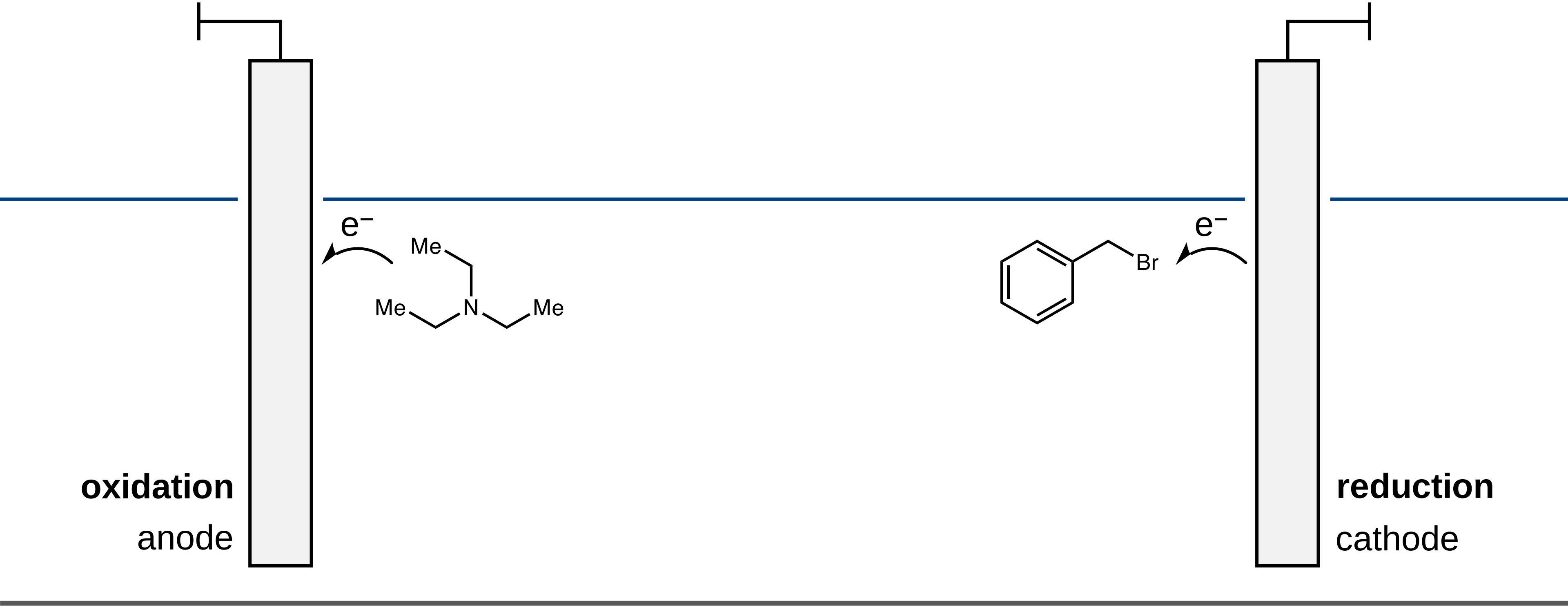
To satisfy the requirement for balanced electron flow, cells often pair a desired reaction at one electrode with an efficient, innocuous reaction at the counter-electrode

Designing an electrochemical cell



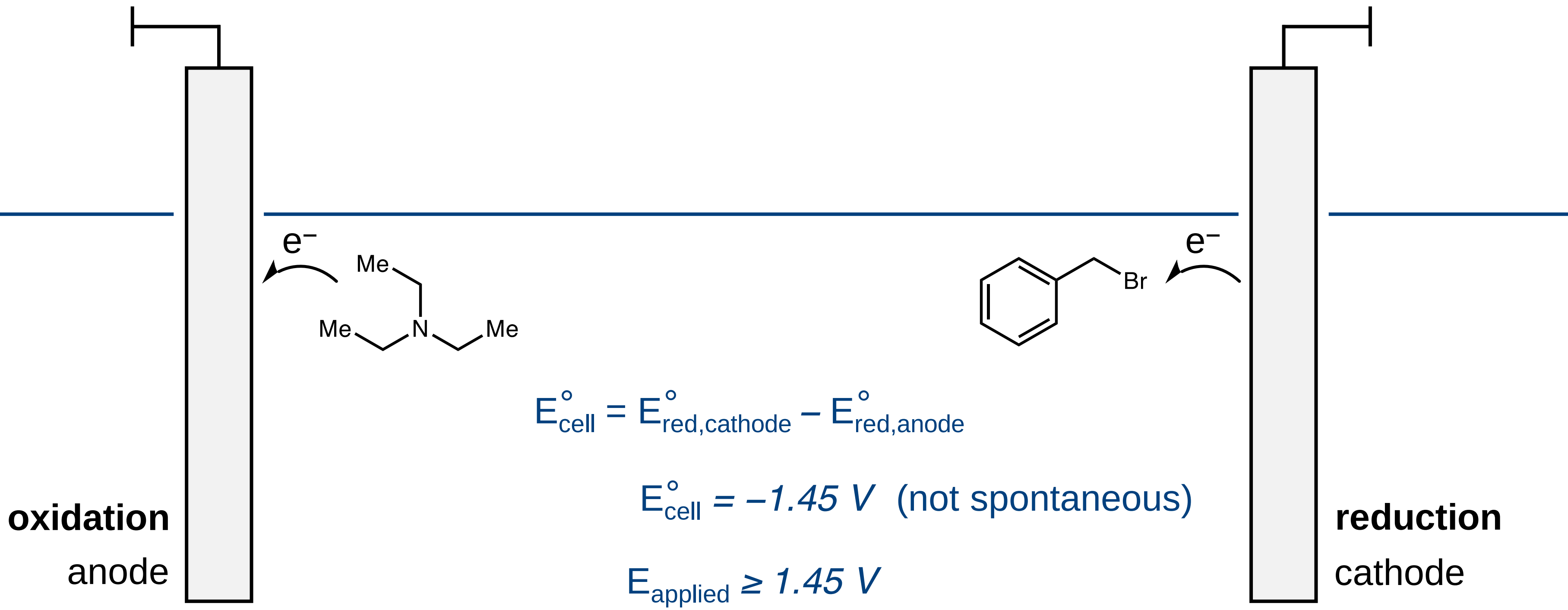
To satisfy the requirement for balanced electron flow, cells often pair a desired reaction at one electrode with an efficient, innocuous reaction at the counter-electrode

Calculating cell potential



The reactions occurring at each electrode in an electrochemical cell determine the **cell potential**

Calculating cell potential

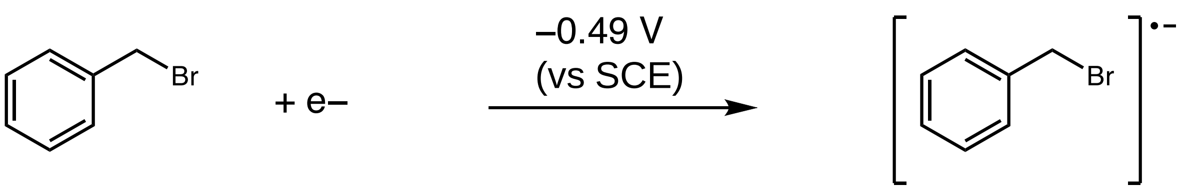


$$E^\circ_{cell} = E^\circ_{red,cathode} - E^\circ_{red,anode}$$

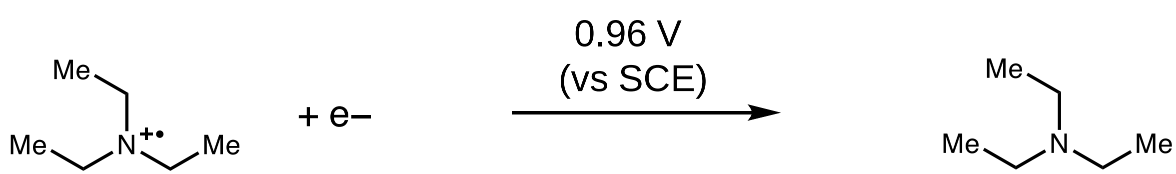
$$E^\circ_{cell} = -1.45\ V \quad \text{(not spontaneous)}$$

$$E_{applied} \geq 1.45\ V$$

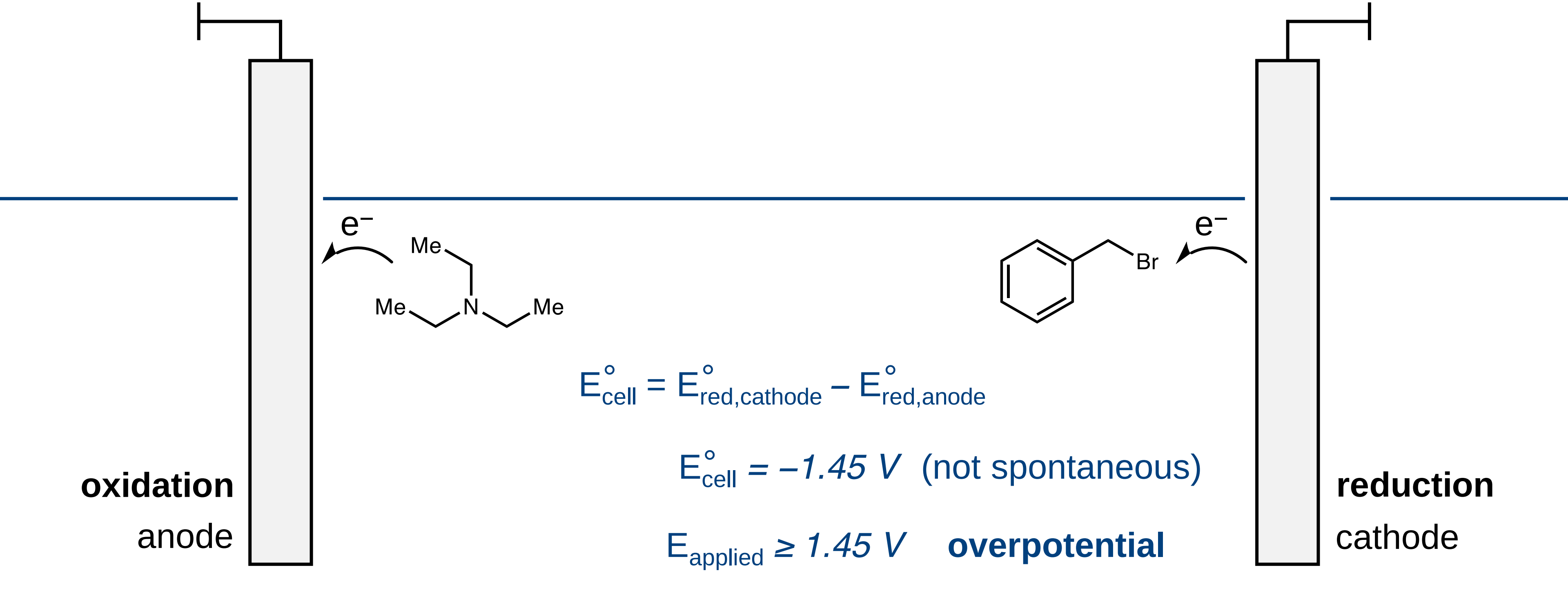
$E^\circ_{red,cathode}$



$E^\circ_{red,anode}$



Calculating cell potential



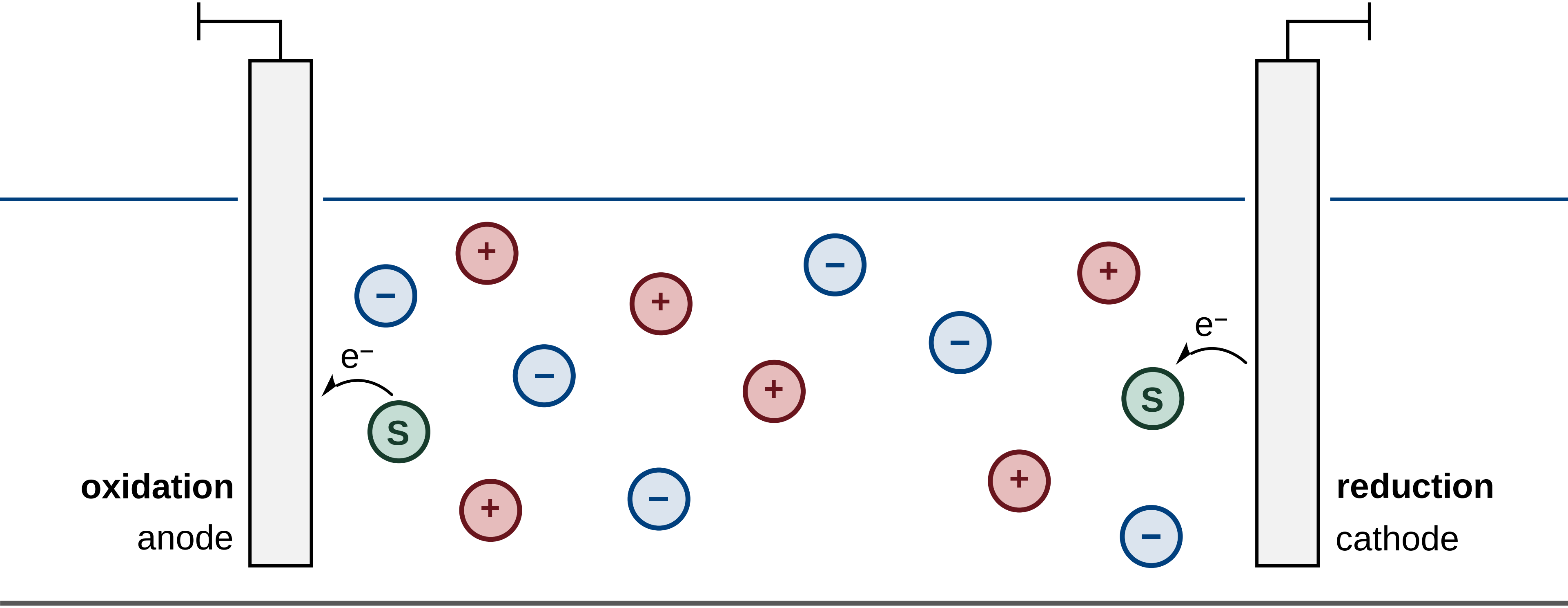
$$E^\circ_{cell} = E^\circ_{red,cathode} - E^\circ_{red,anode}$$

$E^\circ_{cell} = -1.45\ V$ (not spontaneous)

$E_{applied} \geq 1.45\ V$ **overpotential**

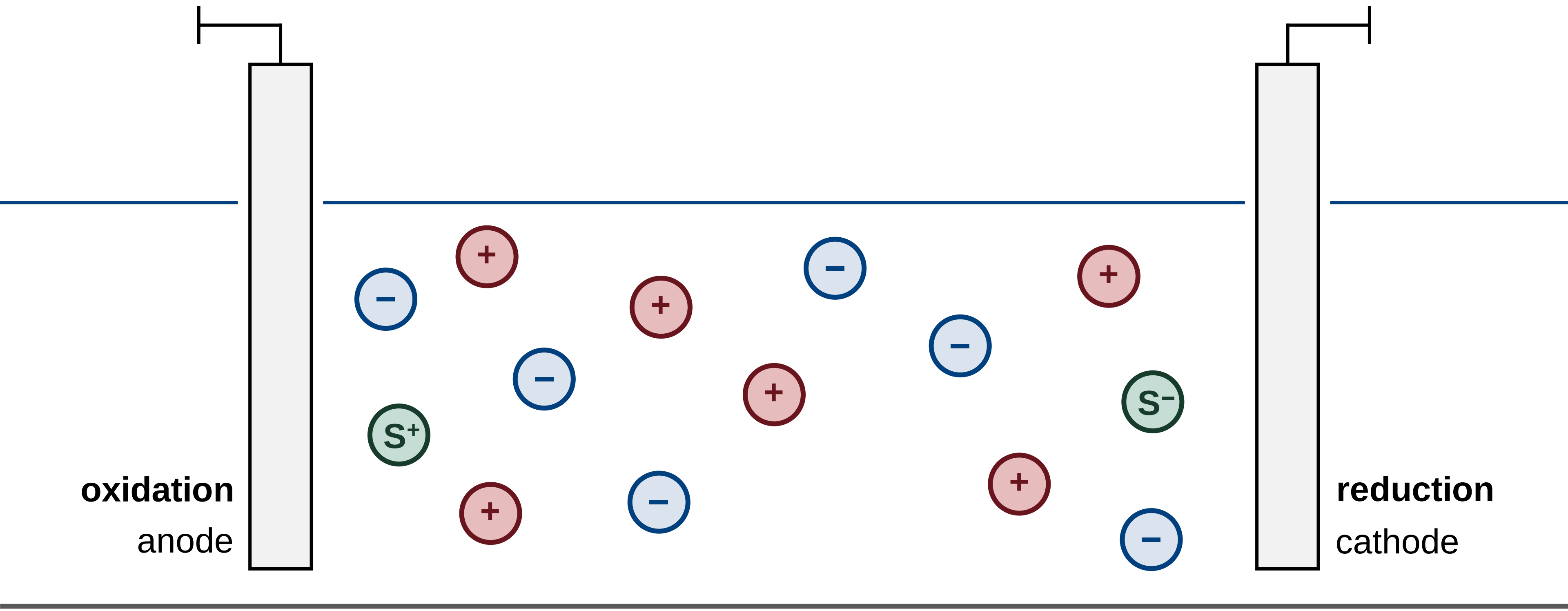
overpotential is the excess energy needed to drive a reaction beyond the thermodynamic minimum, caused by lost energy due to heat generation, inefficiency in electron transfer, etc.

What occurs at the electrode during electrolysis?



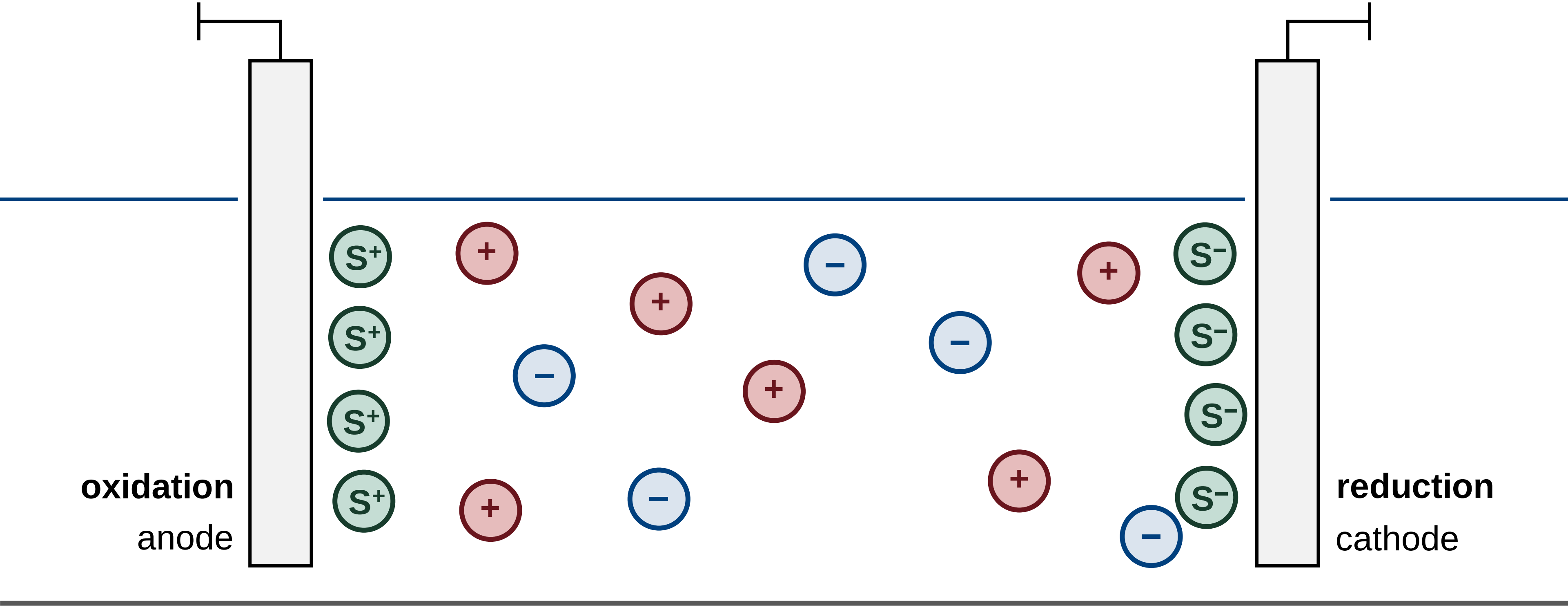
As electrons pass between electrodes and substrate, positively charged species accumulate at the anode and negatively charged species at the cathode

What occurs at the electrode during electrolysis?



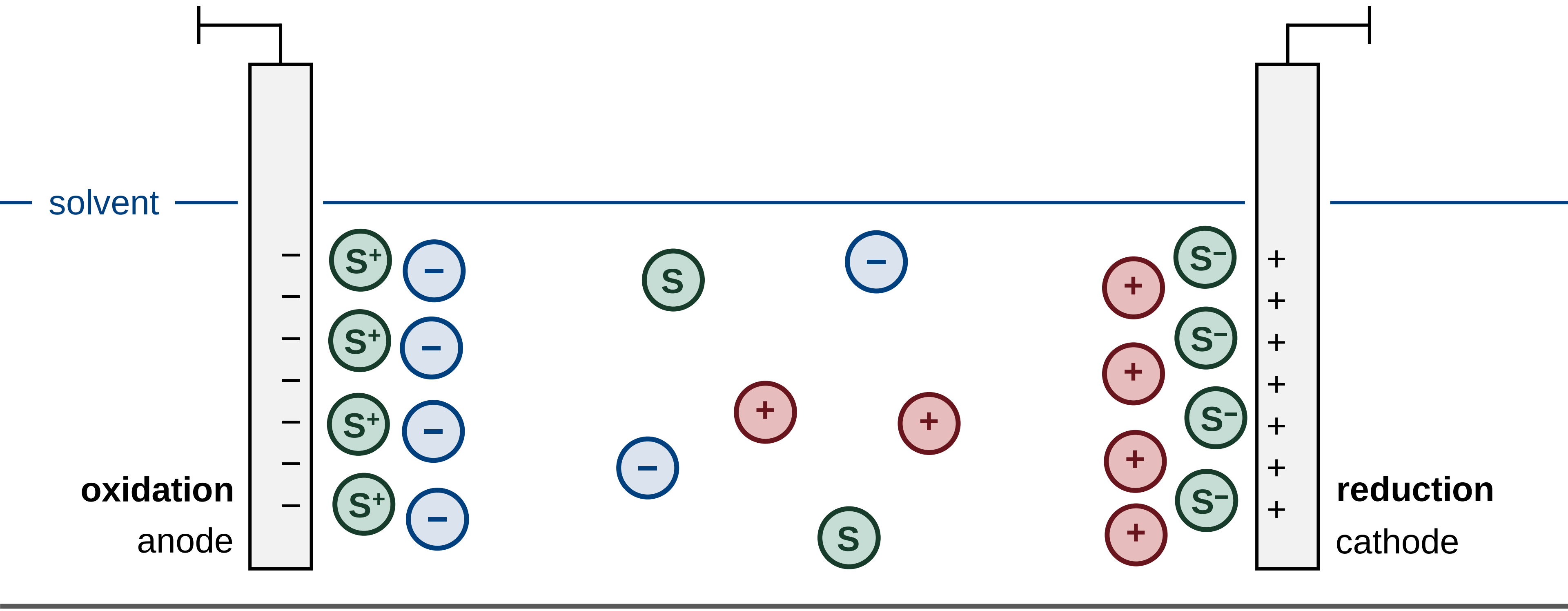
As electrons pass between electrodes and substrate, positively charged species accumulate at the anode and negatively charged species at the cathode

What occurs at the electrode during electrolysis?



As electrons pass between electrodes and substrate, positively charged species accumulate at the anode and negatively charged species at the cathode

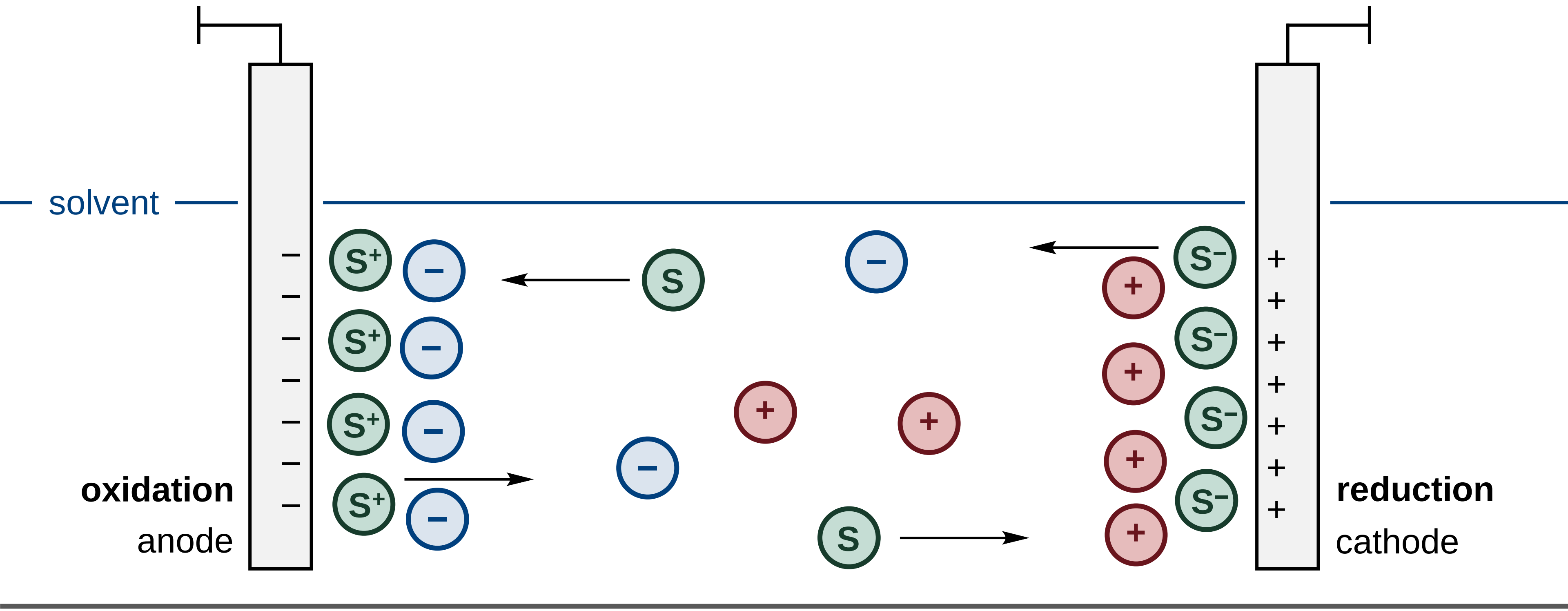
Formation of Helmholtz double layer



Electrolyte diffuses to compensate for the
charge buildup created by the electrical current

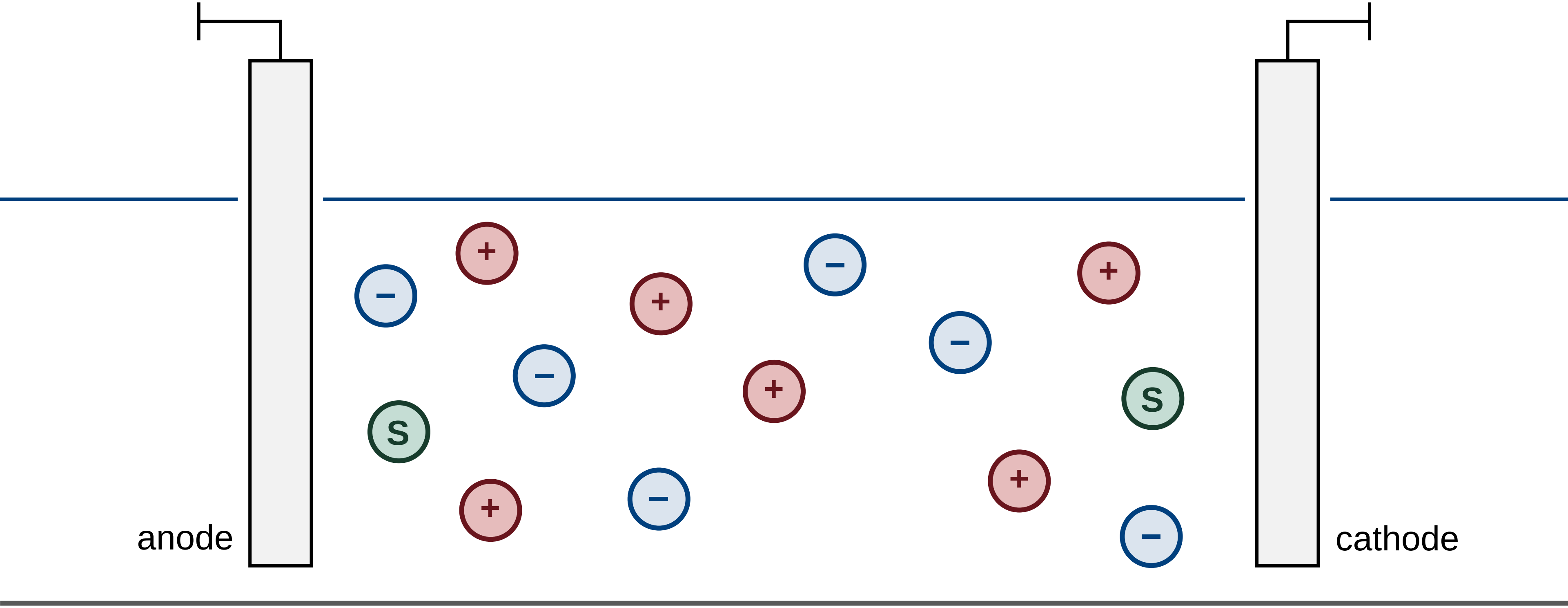
creation of Helmholtz **double layer**

Formation of Helmholtz double layer



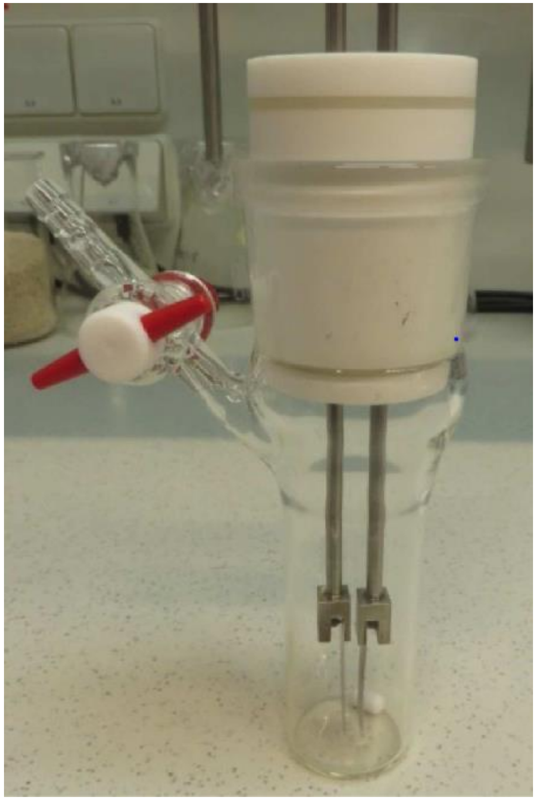
Diffusion (**mass transport**) to and from the electrode can often be rate limiting and important to consider when designing a reaction

Types of electrochemical cells: undivided



an **undivided cell** has both the cathode and the anode in the same chamber

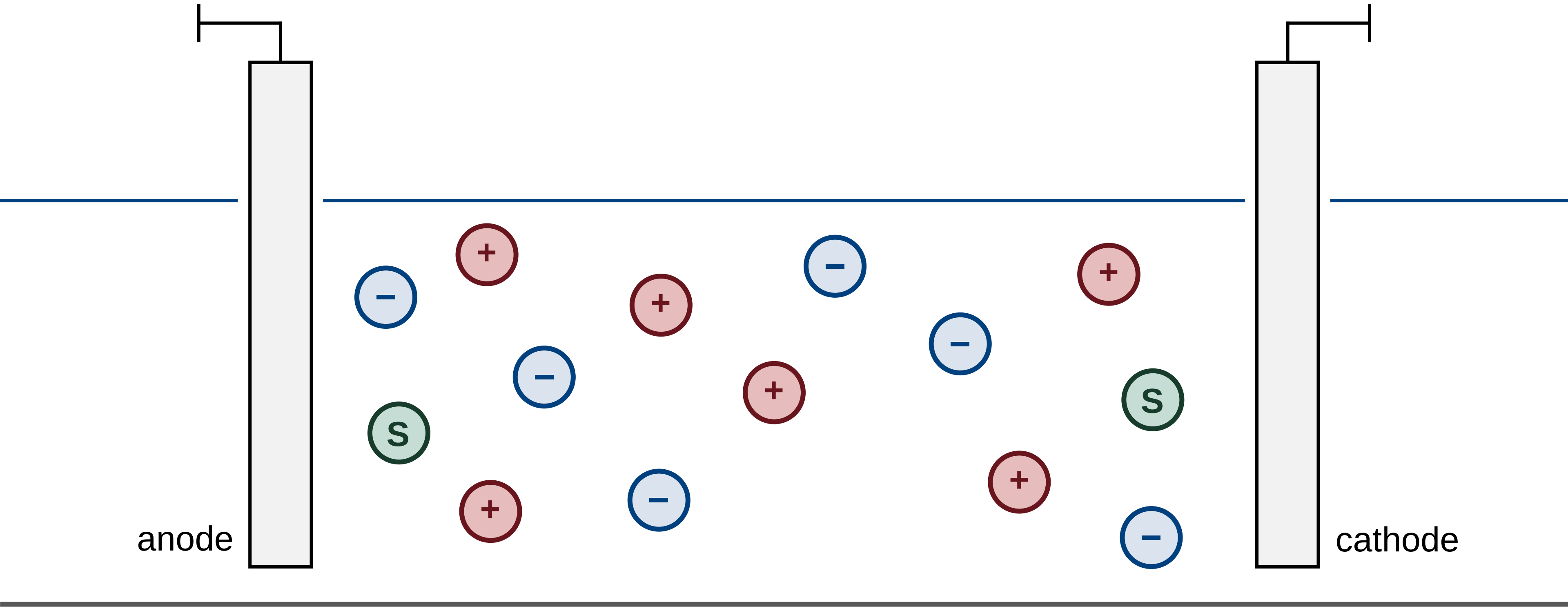
Types of electrochemical cells: undivided



an **undivided cell** has both the cathode and the anode in the same chamber

Hilt, G.. ChemElectroChem. **2020**, 7, 395

Types of electrochemical cells: undivided



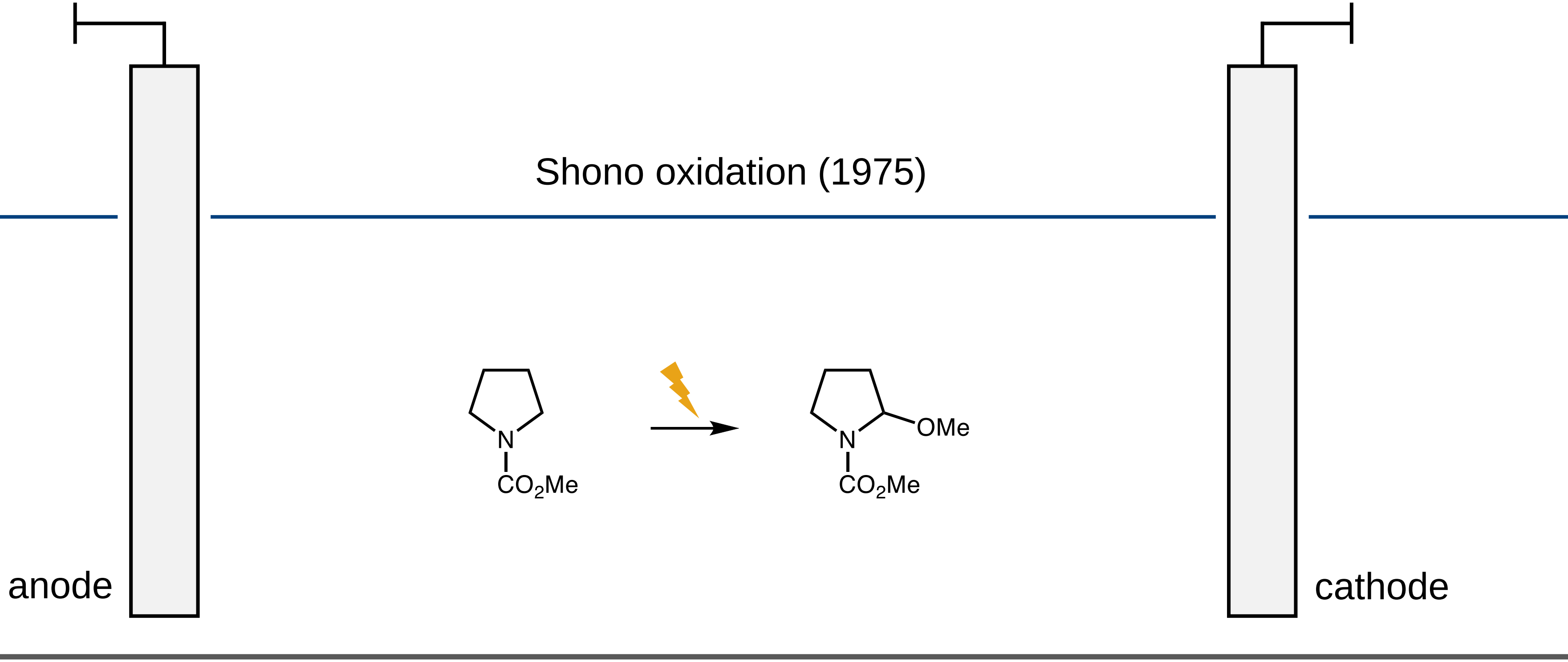
advantages:

- allows substrates to diffuse between electrodes
- can control distance between electrodes
- easy to assemble

disadvantages:

- potential for unwanted side-reactions at counter electrode

Types of electrochemical cells: undivided



Shono, T.; Hamaguchi, H.; Matsumura, Y. J. Am. Chem. Soc. **1975**, 97, 4264

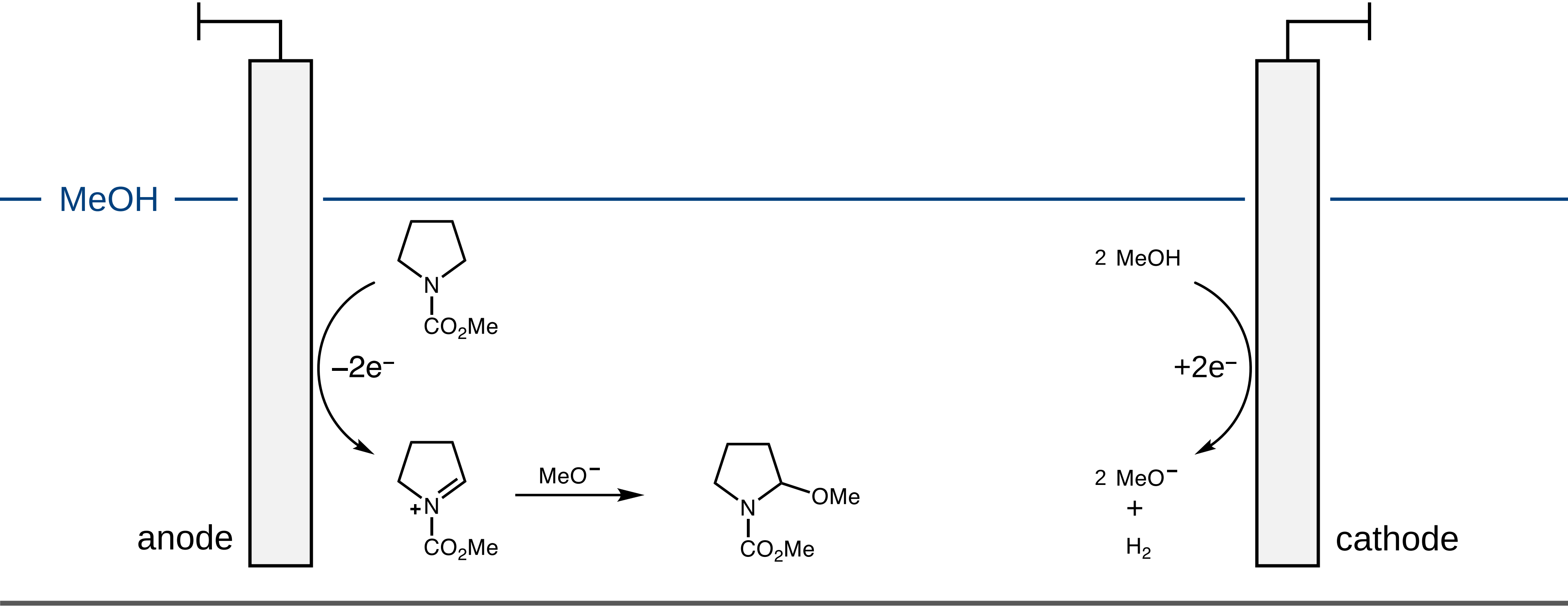
Types of electrochemical cells: undivided

Shono, T.; Hamaguchi, H.; Matsumura, Y. J. Am. Chem. Soc. **1975**, 97, 4264

Types of electrochemical cells: undivided

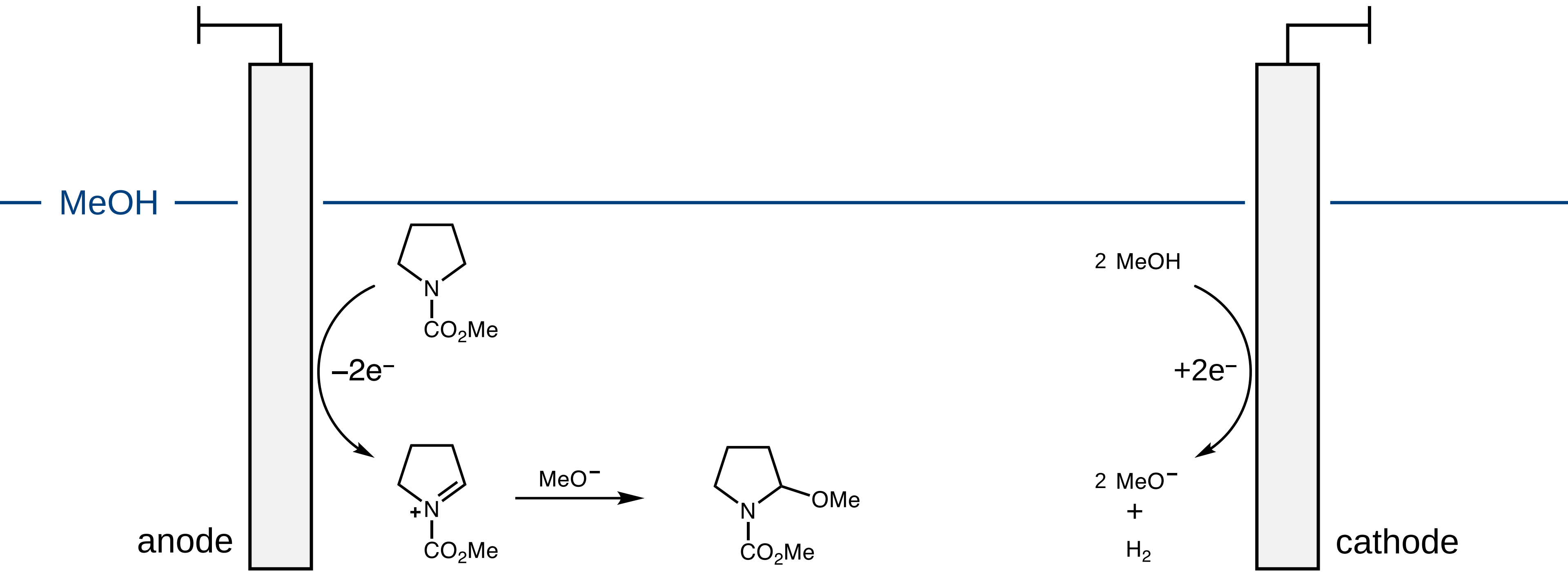
Shono, T.; Hamaguchi, H.; Matsumura, Y. J. Am. Chem. Soc. **1975**, 97, 4264

Types of electrochemical cells: undivided



Shono, T.; Hamaguchi, H.; Matsumura, Y. J. Am. Chem. Soc. **1975**, 97, 4264

Types of electrochemical cells: undivided



advantages:

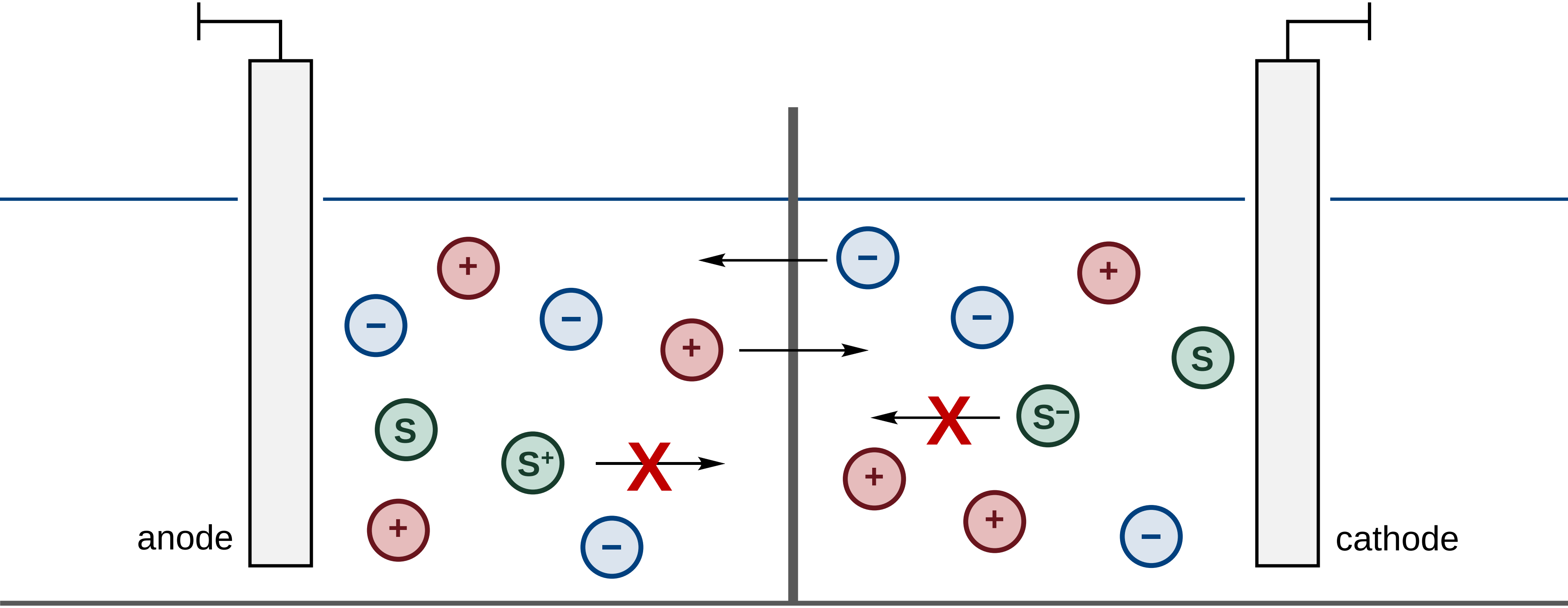
- ☐ allows substrates to **diffuse between electrodes**
- ☐ can control distance between electrodes
- ☐ easy to assemble

disadvantages:

- ☐ potential for unwanted side-reactions at counter electrode

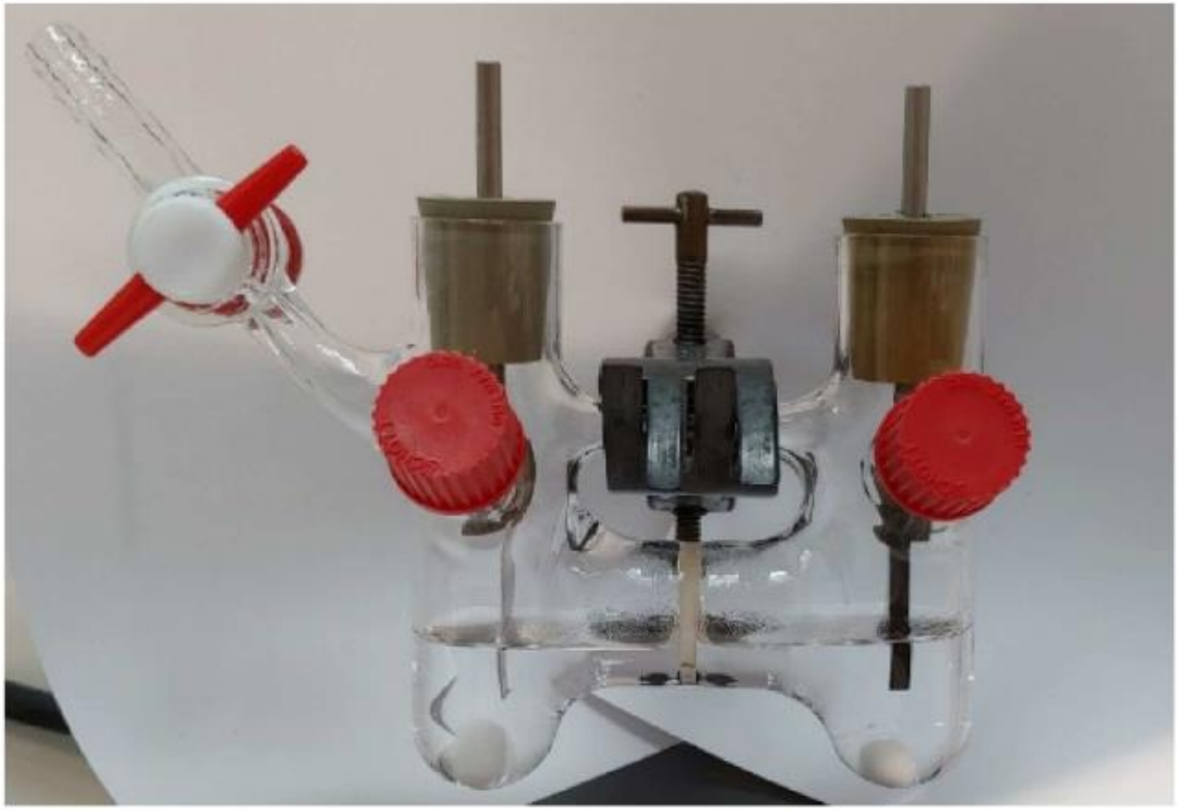
Shono, T.; Hamaguchi, H.; Matsumura, Y. J. Am. Chem. Soc. **1975**, 97, 4264

Types of electrochemical cells: divided



a **divided cell** separates the cathode and the anode with a membrane that is porous to ions, but not substrates

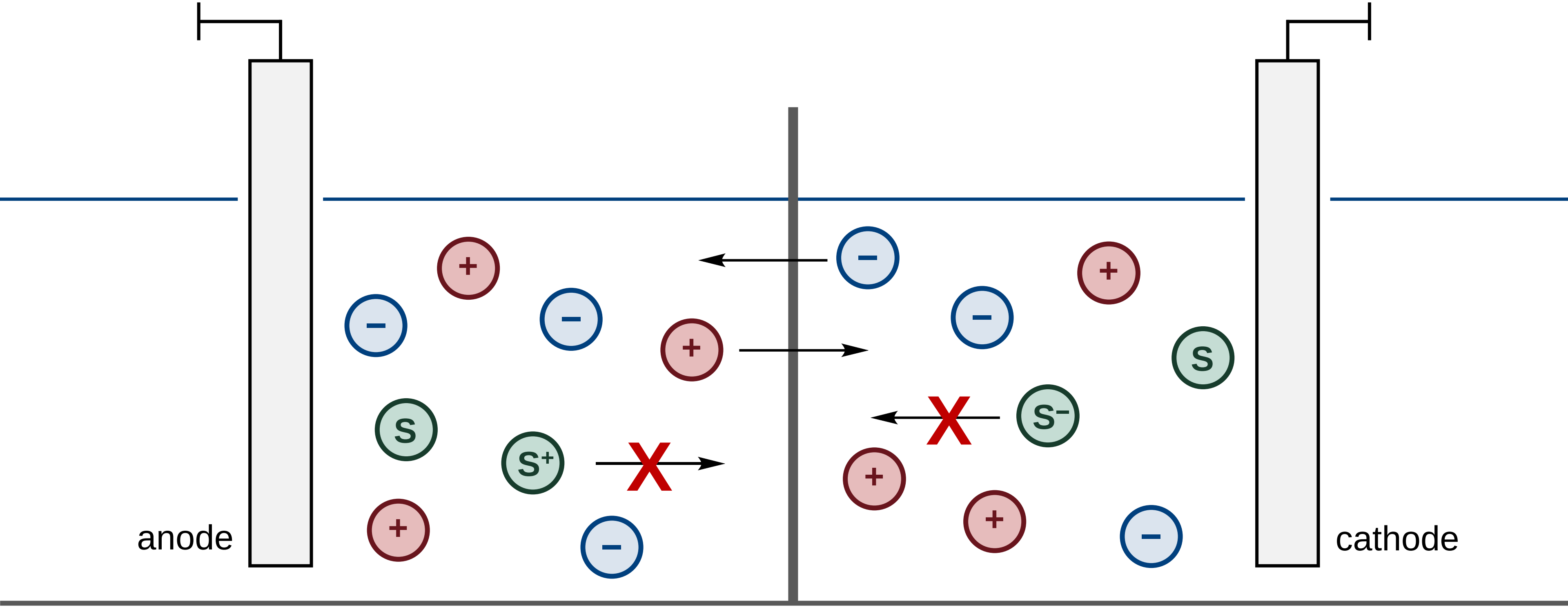
Types of electrochemical cells: divided



a **divided cell** separates the cathode and the anode with a membrane that is porous to ions, but not substrates

Hilt, G.. ChemElectroChem. **2020**, 7, 395

Types of electrochemical cells: divided



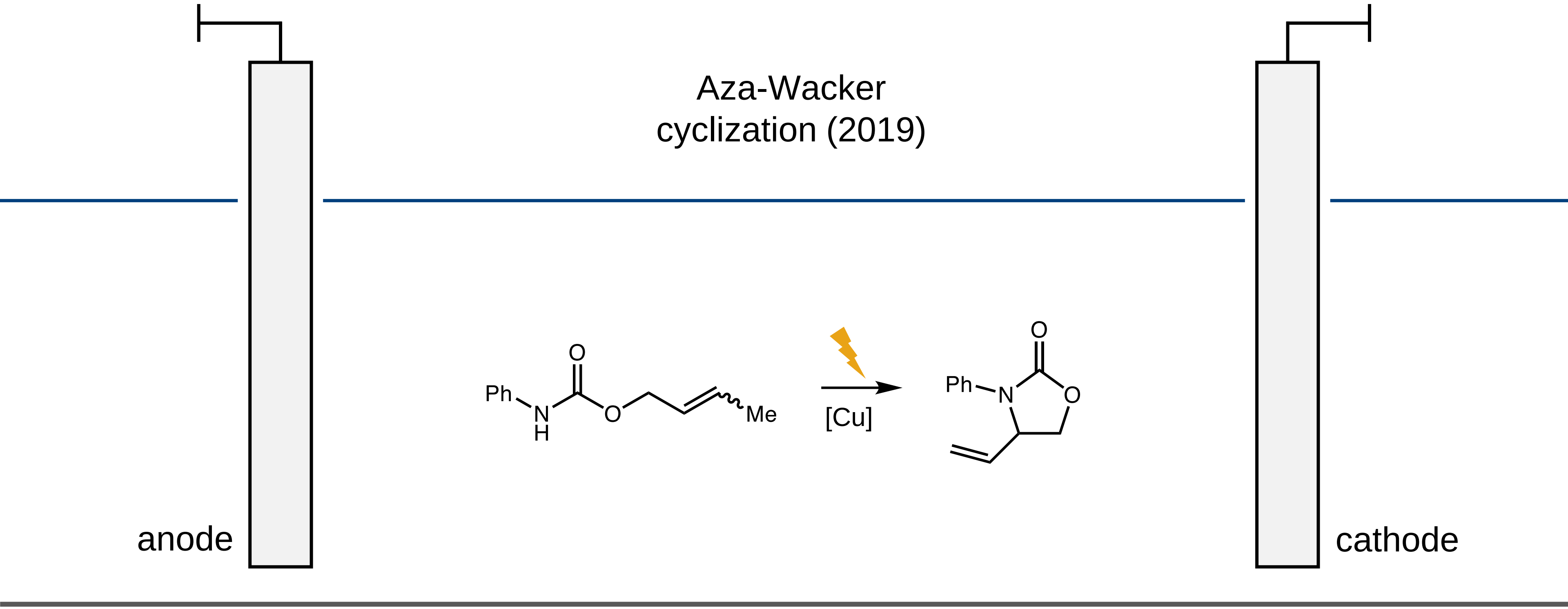
advantages:

- ☐ creates a unique environment at each electrode
- ☐ can prevent unwanted side reactions

disadvantages:

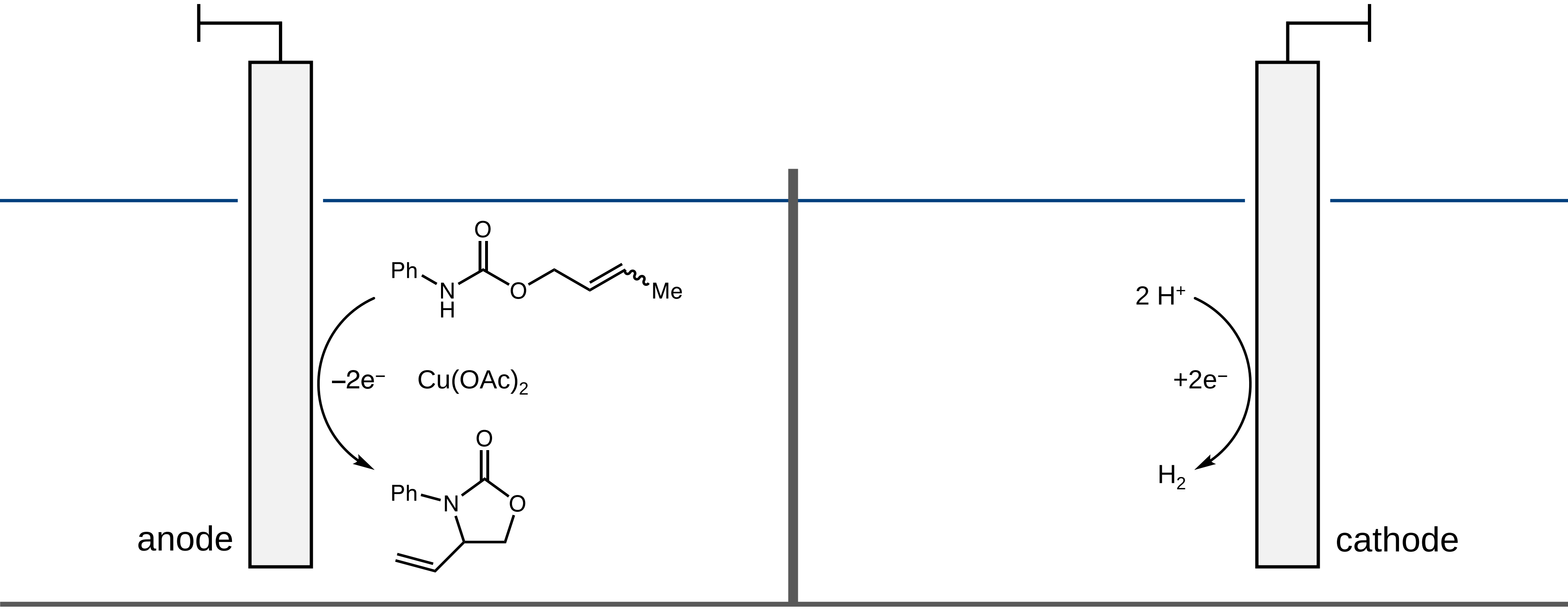
- ☐ cells typically possess high resistance
- ☐ can display slower reaction rate
- ☐ challenging/expensive to assemble

Types of electrochemical cells: divided



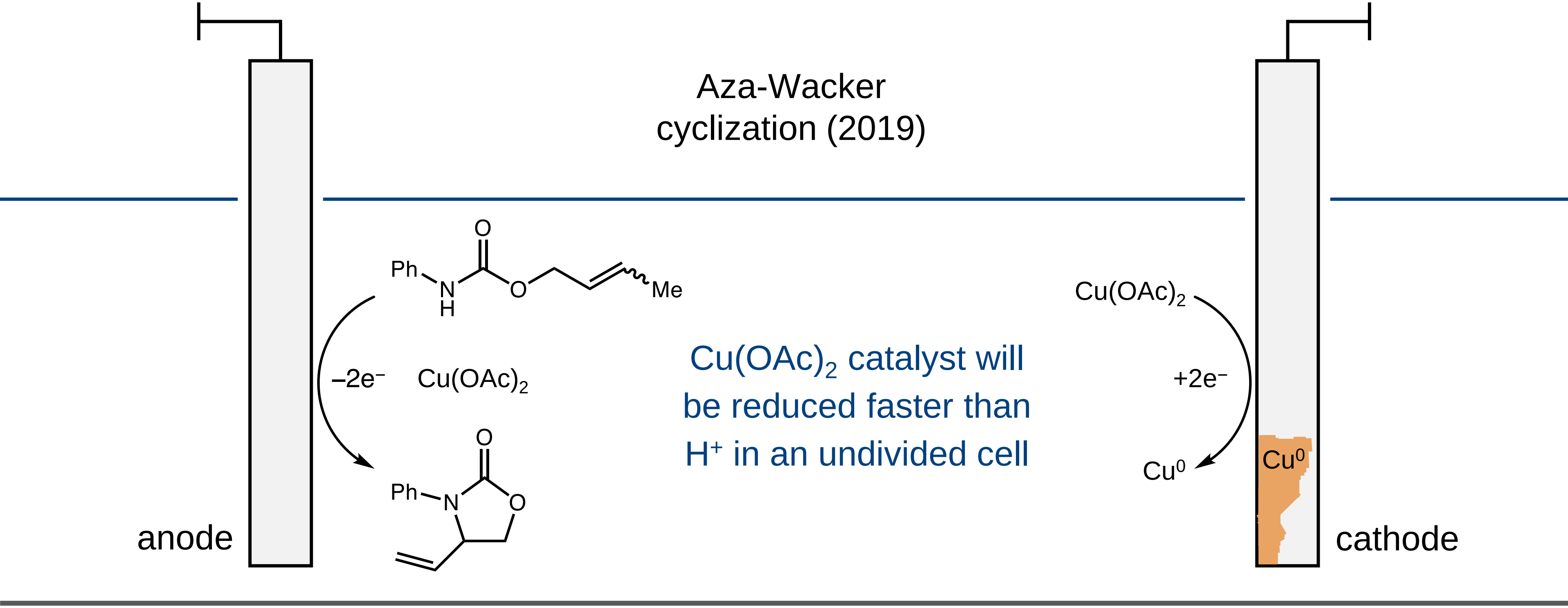
Yi, X.; Hu, X. Angew. Chem. Int. Ed. **2019**, 58, 4700

Types of electrochemical cells: divided



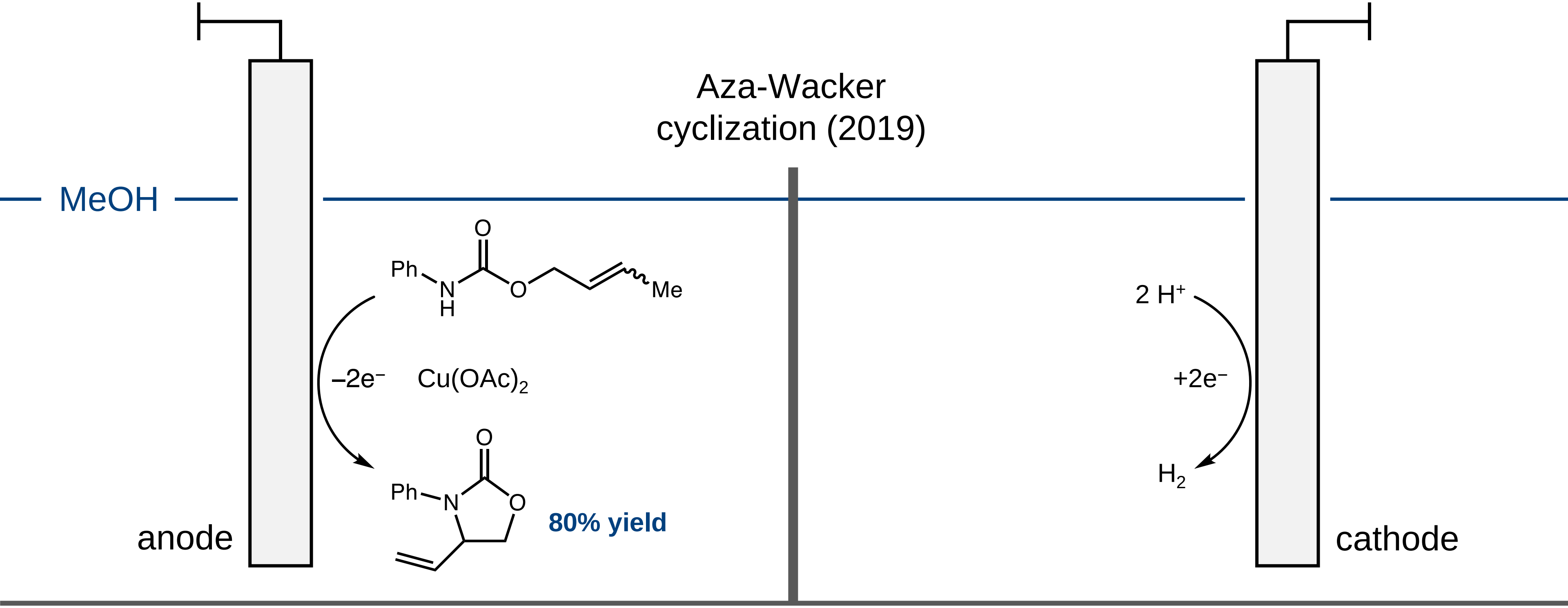
Yi, X.; Hu, X. Angew. Chem. Int. Ed. **2019**, 58, 4700

Types of electrochemical cells: divided



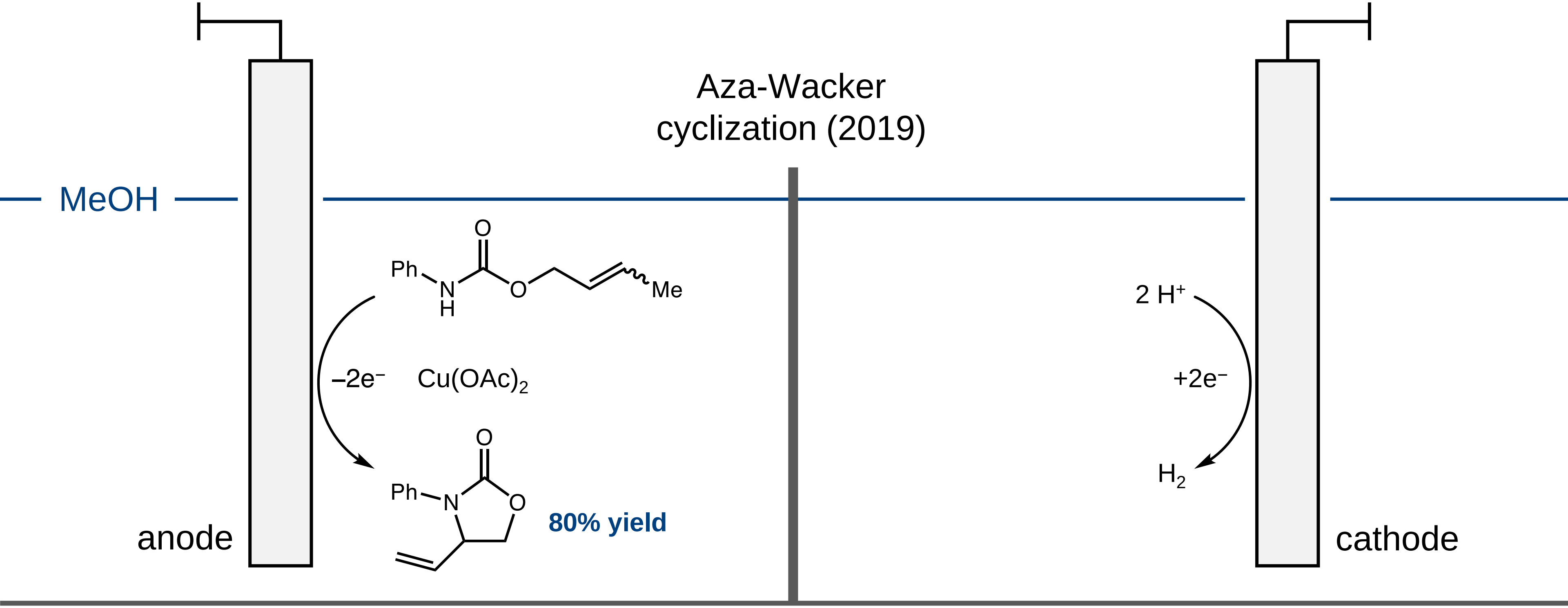
Yi, X.; Hu, X. Angew. Chem. Int. Ed. **2019**, 58, 4700

Types of electrochemical cells: divided



Yi, X.; Hu, X. Angew. Chem. Int. Ed. **2019**, 58, 4700

Types of electrochemical cells: divided



advantages:

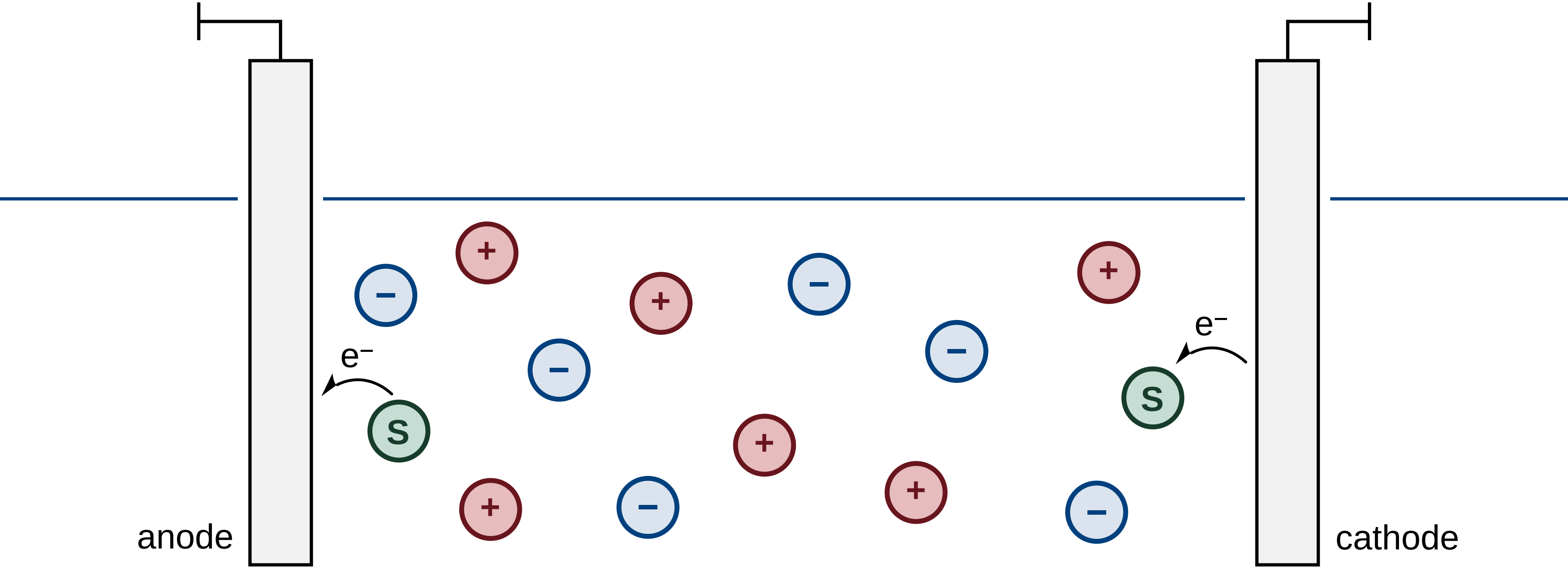
- ☐ creates a unique environment at each electrode
- ☐ can **prevent unwanted side reactions**

disadvantages:

- ☐ cells typically possess high resistance
- ☐ can display slower reaction rate
- ☐ challenging/expensive to assemble

Yi, X.; Hu, X. Angew. Chem. Int. Ed. **2019**, 58, 4700

Electrode materials



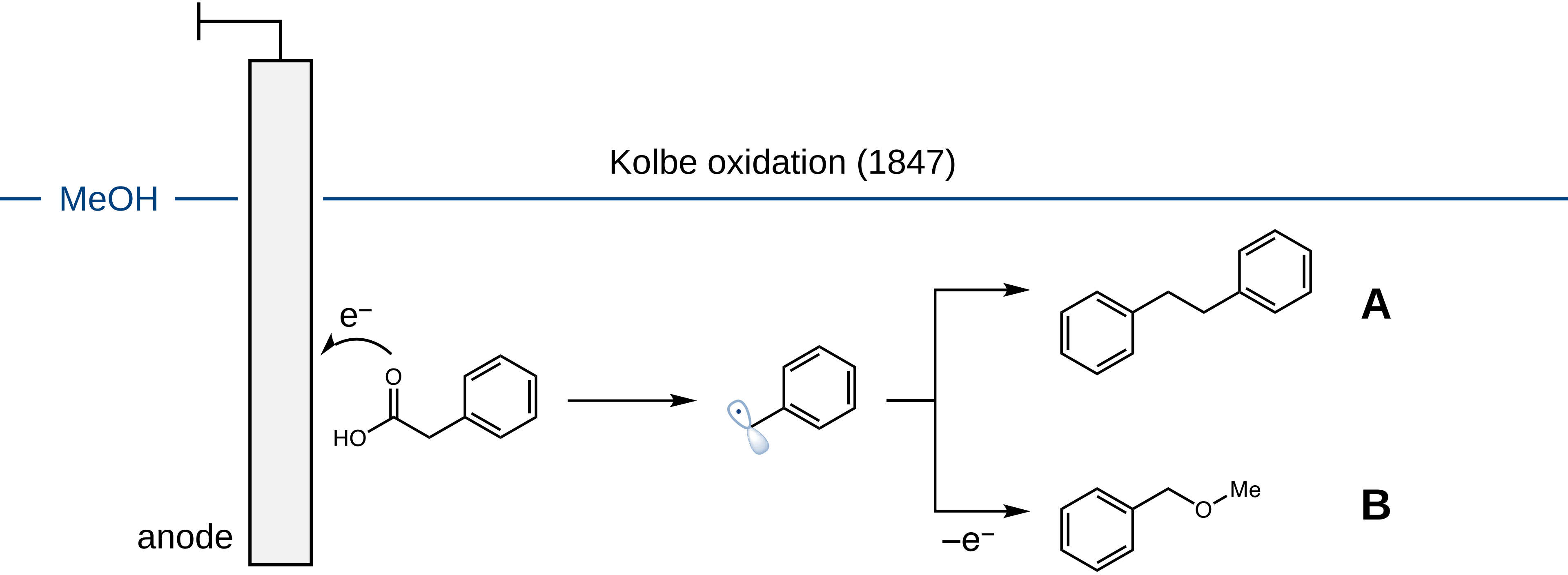
common electrodes:

glassy carbon	nickel foam
graphite	lead
RVC (porous carbon)	platinum

electrode choice is often empirical, but it imparts a significant effect on the kinetics and thermodynamics of electron transfer

Heard, D. M.; Lennox, A. J. J. Angew. Chem. Int. Ed. **2020**, 59, 18866

Electrode materials



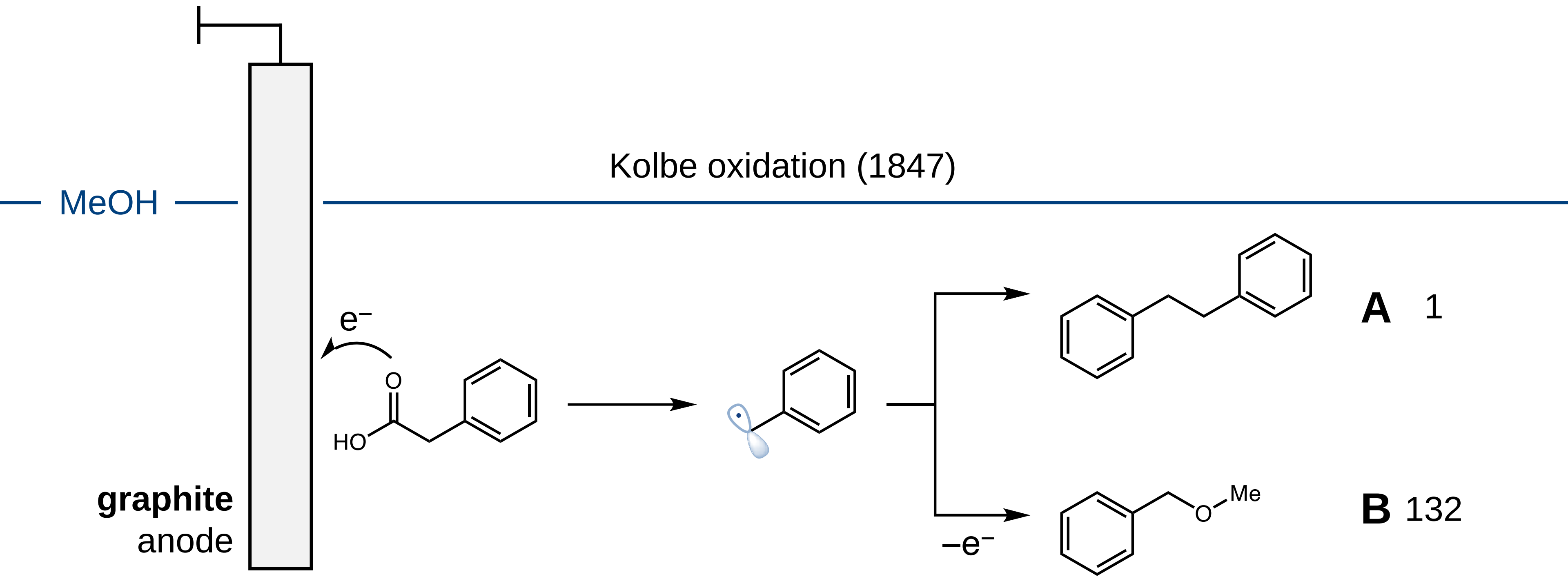
common electrodes:

glassy carbon	nickel foam
graphite	lead
RVC (porous carbon)	platinum

electrode choice is often empirical, but it imparts a significant effect on the kinetics and thermodynamics of electron transfer

Ross, S. D.; Finkelstein, M. J. Org. Chem. **1969**, 34, 2923

Electrode materials



common electrodes:

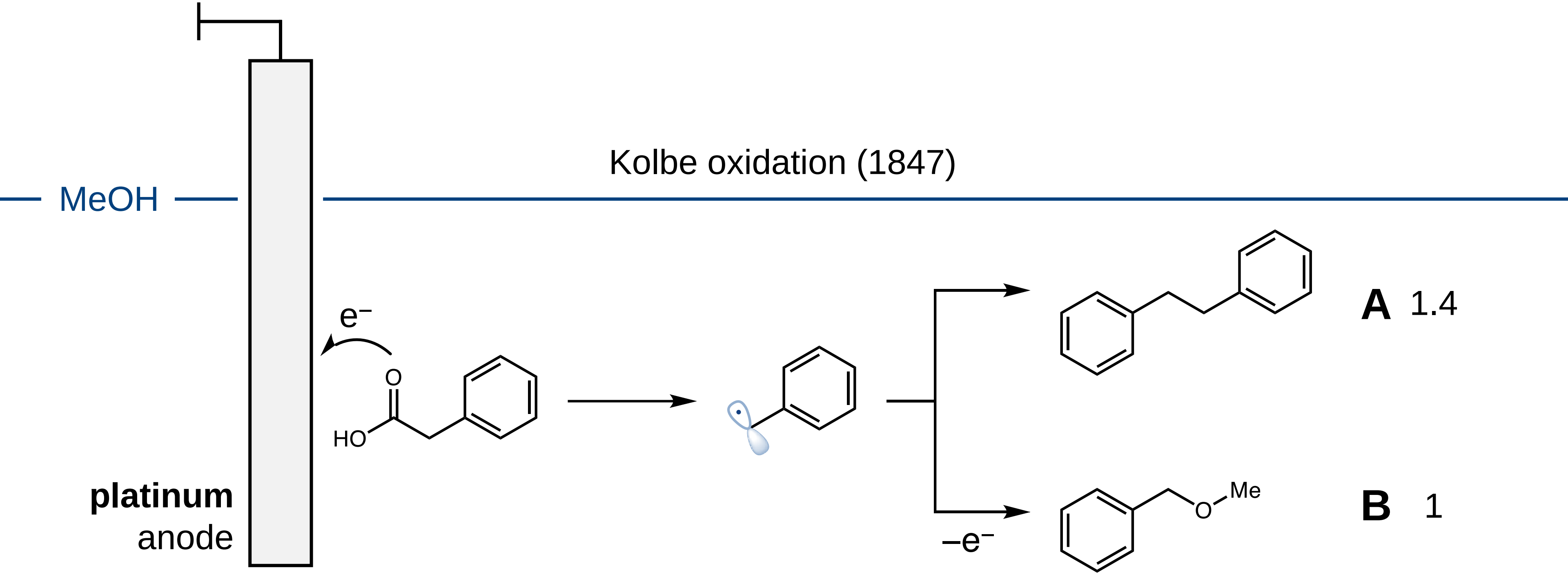
glassy carbon	nickel foam
graphite	lead
RVC (porous carbon)	platinum

graphite 1 : 132 (A : B)

radicals formed at graphite electrode adsorb onto carbon, promoting second oxidation; radicals formed at Pt are free to diffuse

Ross, S. D.; Finkelstein, M. J. Org. Chem. **1969**, 34, 2923

Electrode materials



common electrodes:

glassy carbon	nickel foam
graphite	lead
RVC (porous carbon)	platinum

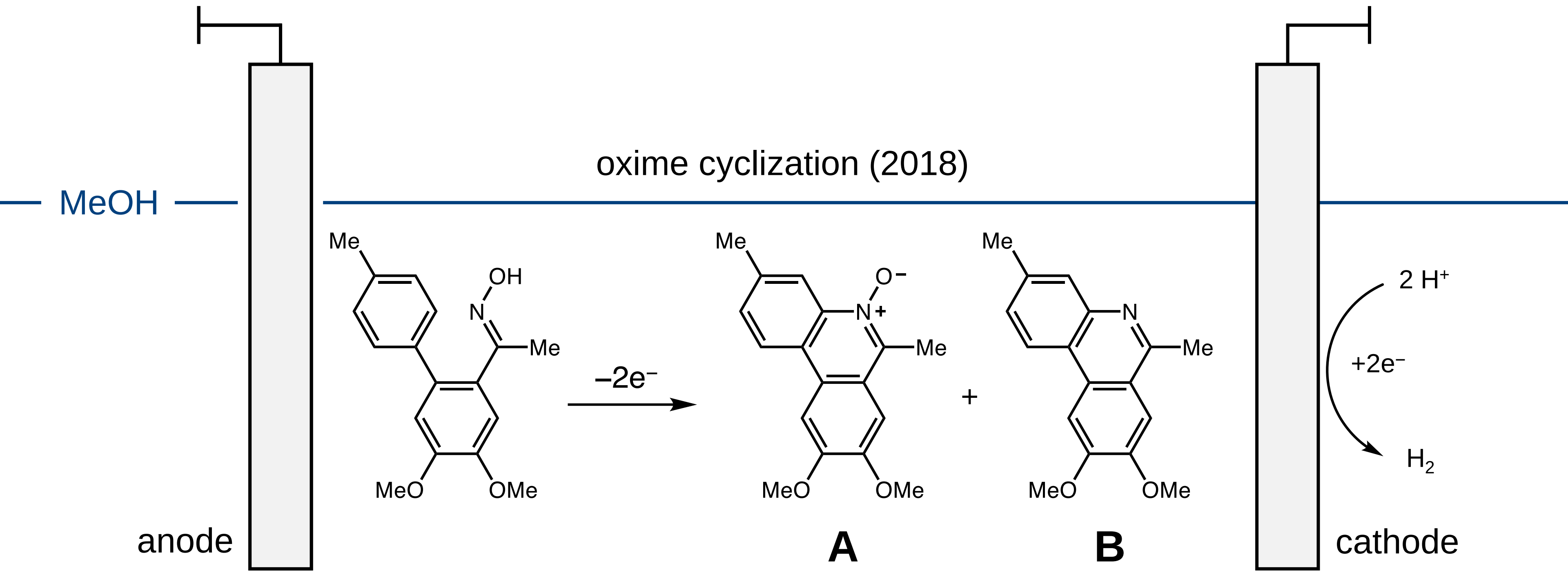
graphite 1 : 132 (A : B)

platinum 1.4 : 1 (A : B)

radicals formed at graphite electrode adsorb onto carbon, promoting second oxidation; radicals formed at Pt are free to diffuse

Ross, S. D.; Finkelstein, M. J. Org. Chem. **1969**, 34, 2923

Electrode materials



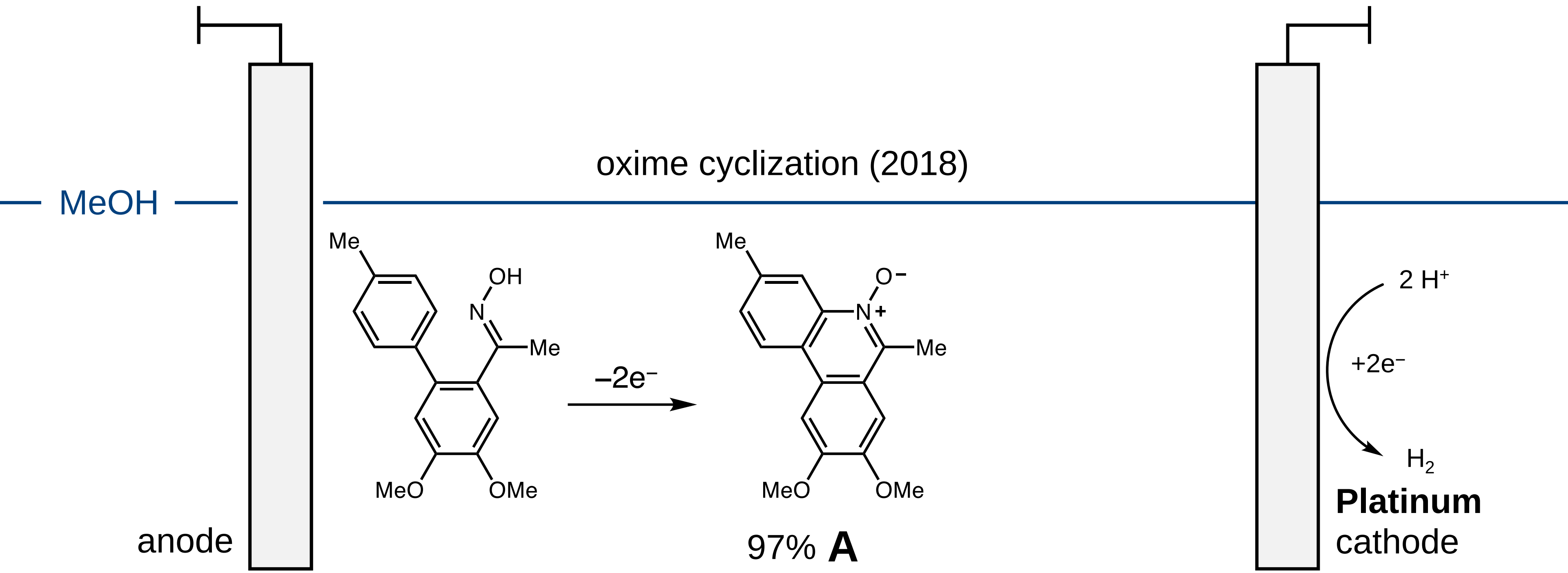
common electrodes:

glassy carbon	nickel foam
graphite	lead
RVC (porous carbon)	platinum

electrode choice is often empirical, but it imparts a significant effect on the kinetics and thermodynamics of electron transfer

Zhao, H.-B.; Xu, P.; Song, J.; Xu, H.-C. Angew. Chem. Int. Ed. **2018**, 57, 15153

Electrode materials



common electrodes:

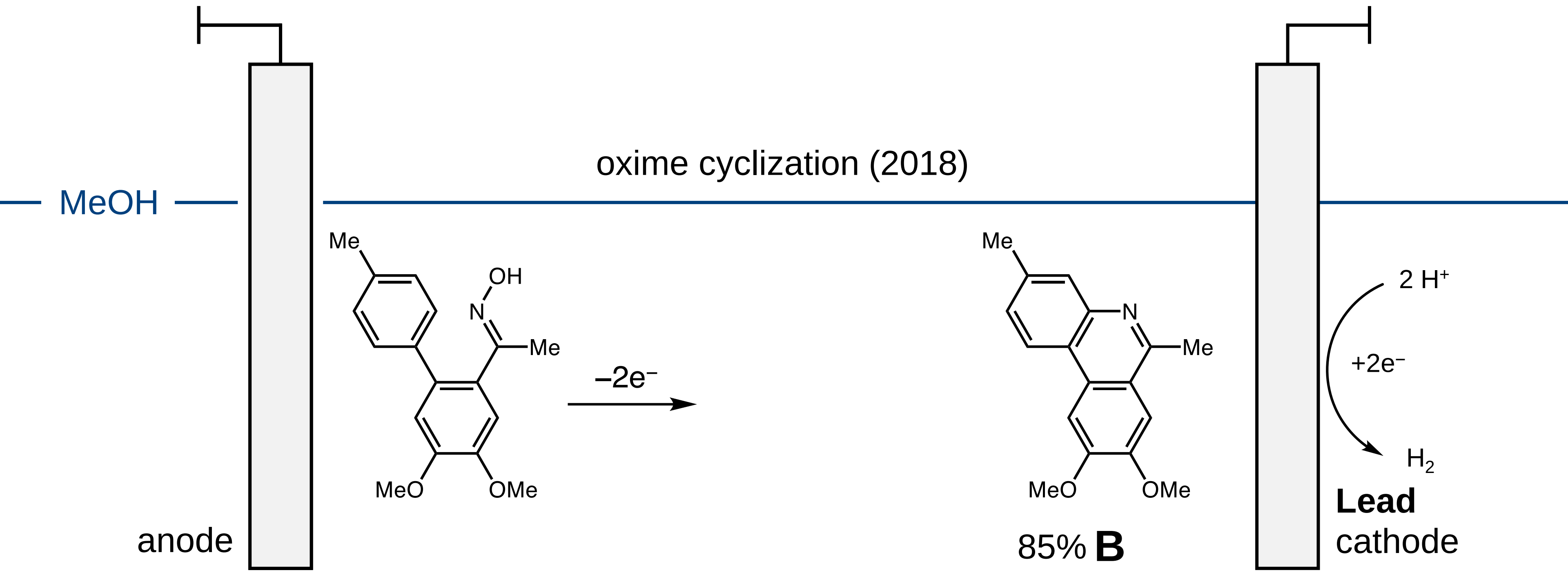
glassy carbon	nickel foam
graphite	lead
RVC (porous carbon)	platinum

platinum cathode 97% **A**

Cathode controls the overpotential for H_2 reduction; for Pt, H_2 is reduced before product, while for Pb the product is reduced first

Zhao, H.-B.; Xu, P.; Song, J.; Xu, H.-C. Angew. Chem. Int. Ed. **2018**, 57, 15153

Electrode materials



common electrodes:

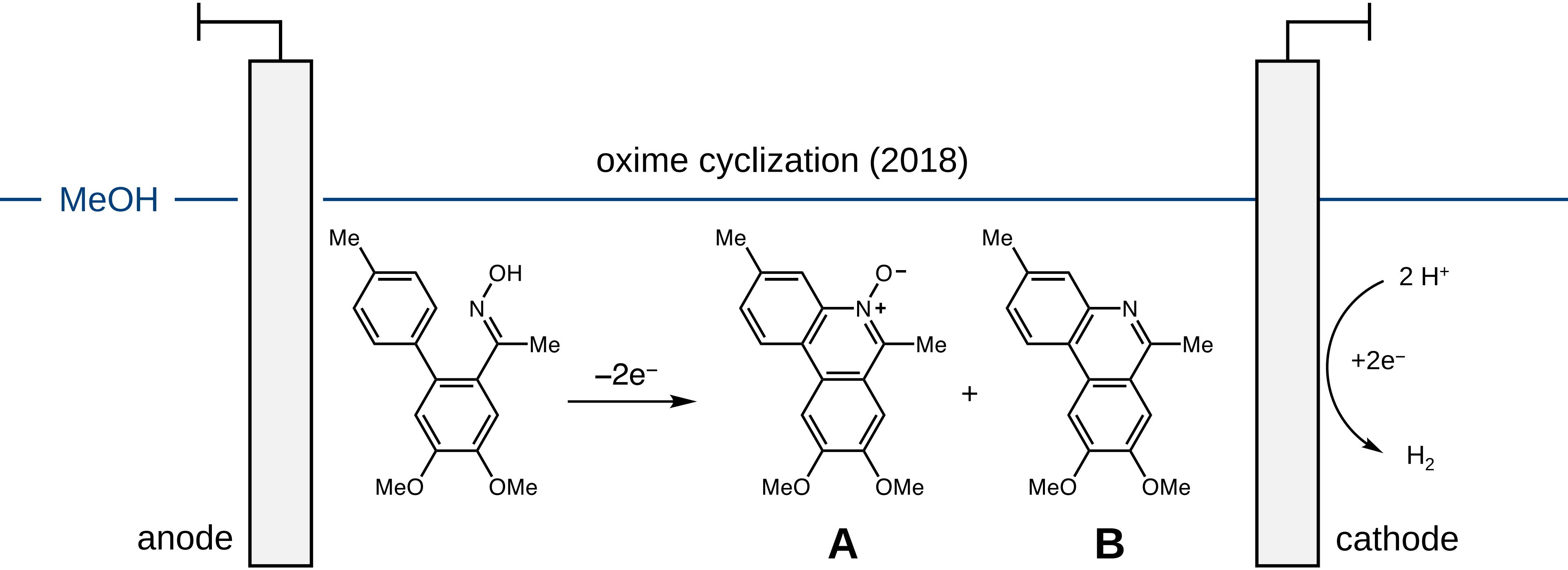
glassy carbon	nickel foam
graphite	lead
RVC (porous carbon)	platinum

platinum cathode	97% **A**
lead cathode	85% **B**

Cathode controls the overpotential for H_2 reduction; for Pt, H_2 is reduced before product, while for Pb the product is reduced first

Zhao, H.-B.; Xu, P.; Song, J.; Xu, H.-C. Angew. Chem. Int. Ed. **2018**, 57, 15153

Electrode materials



common electrodes:

glassy carbon	nickel foam
graphite	lead
RVC (porous carbon)	platinum

platinum cathode	97% **A**
lead cathode	85% **B**

overpotential for H_2 reduction

Hg > Pb > graphite > Cu > Fe, Ni > Co > Pd, Pt

Zhao, H.-B.; Xu, P.; Song, J.; Xu, H.-C. Angew. Chem. Int. Ed. **2018**, 57, 15153

Sacrificial anodes

common sacrificial anodes:

zinc

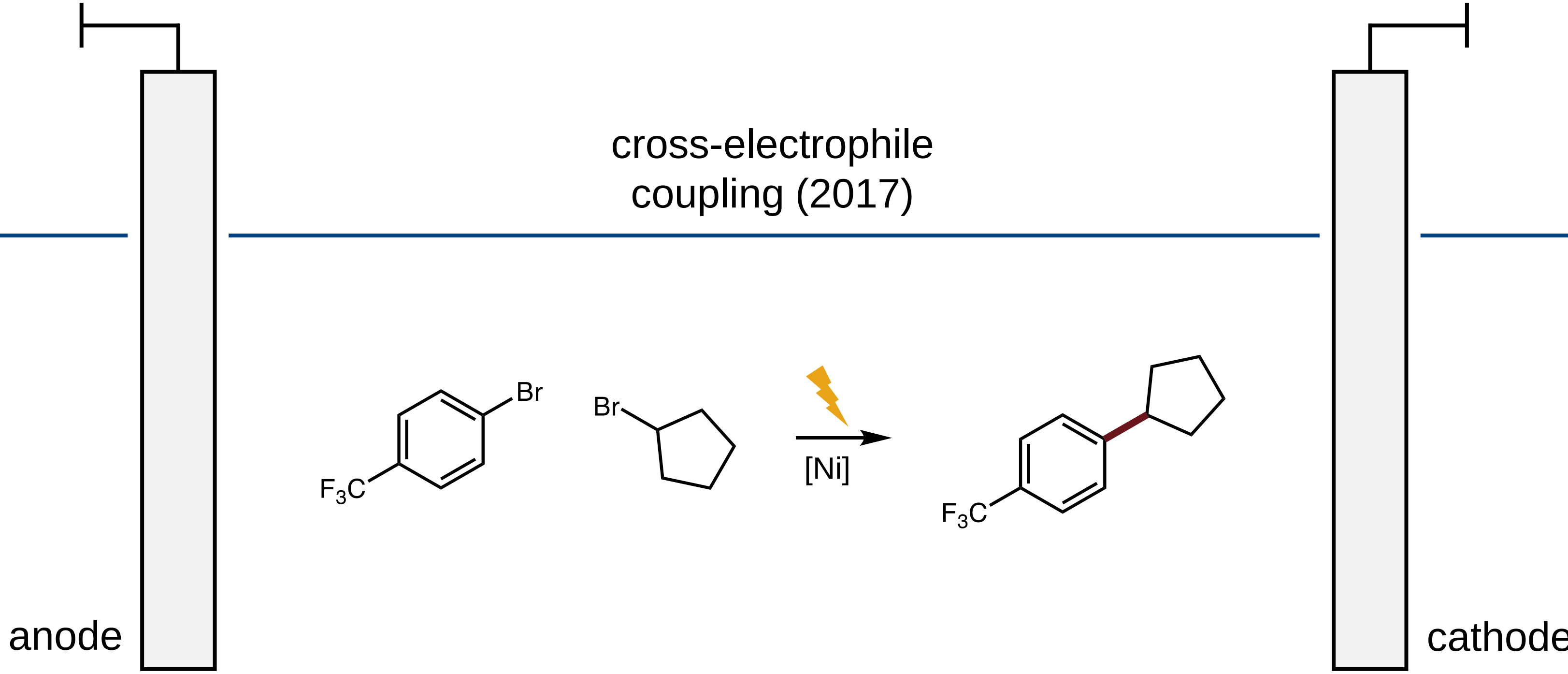
magnesium

aluminum

Sacrificial anodes oxidize themselves, releasing ions into solution and preventing unwanted oxidation processes

Heard, D. M.; Lennox, A. J. J. Angew. Chem. Int. Ed. **2020**, 59, 18866

Sacrificial anodes



common sacrificial anodes:

zinc

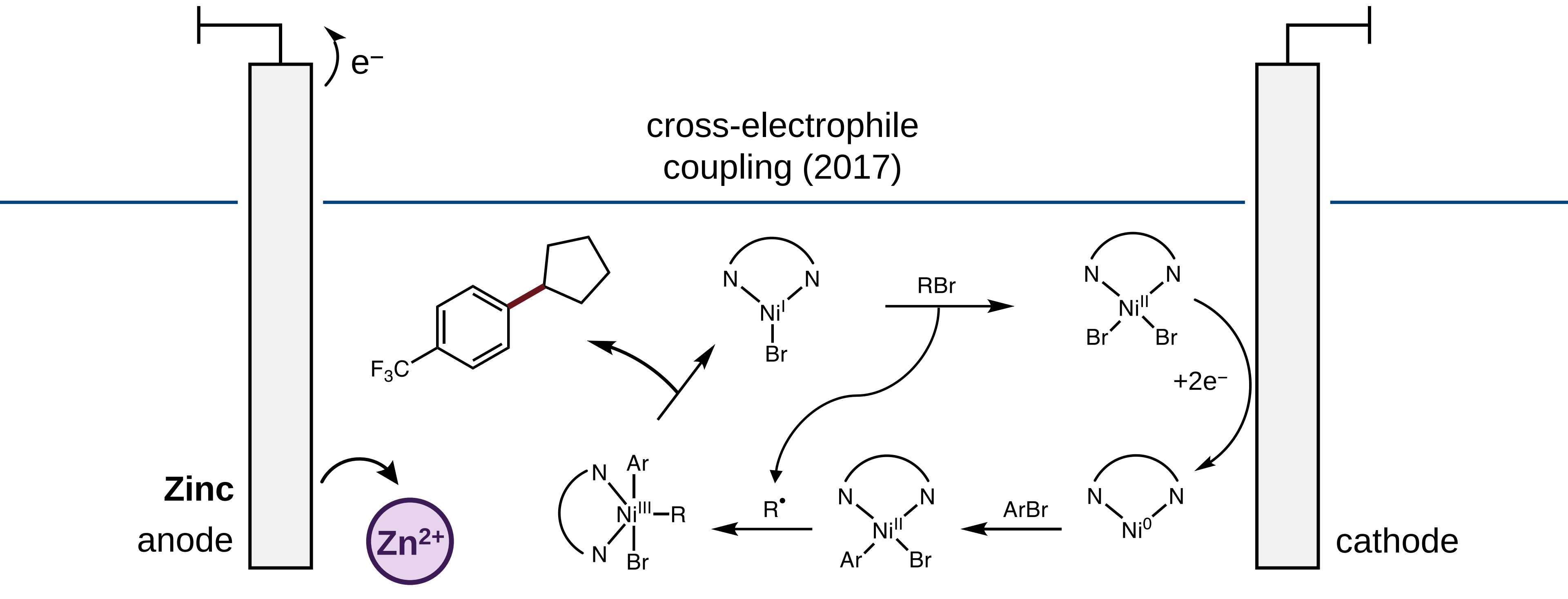
magnesium

aluminum

Sacrificial anodes oxidize themselves, releasing ions into solution and **preventing unwanted oxidation processes**

Perkins, R. J.; Pedro, D. J.; Hansen, E. C. J. Org. Chem. **2017**, 19, 3755

Sacrificial anodes



common sacrificial anodes:

zinc

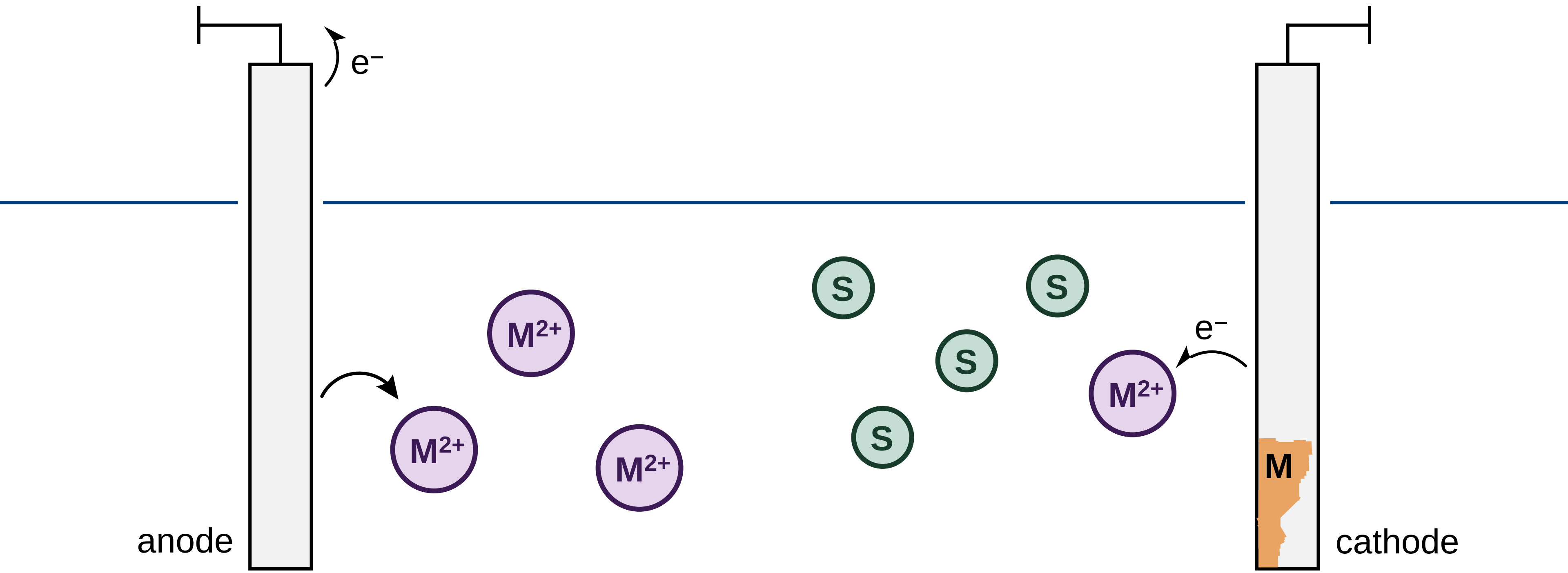
magnesium

aluminum

Sacrificial anodes oxidize themselves, releasing ions into solution and **preventing unwanted oxidation processes**

Perkins, R. J.; Pedro, D. J.; Hansen, E. C. J. Org. Chem. **2017**, 19, 3755

Sacrificial anodes

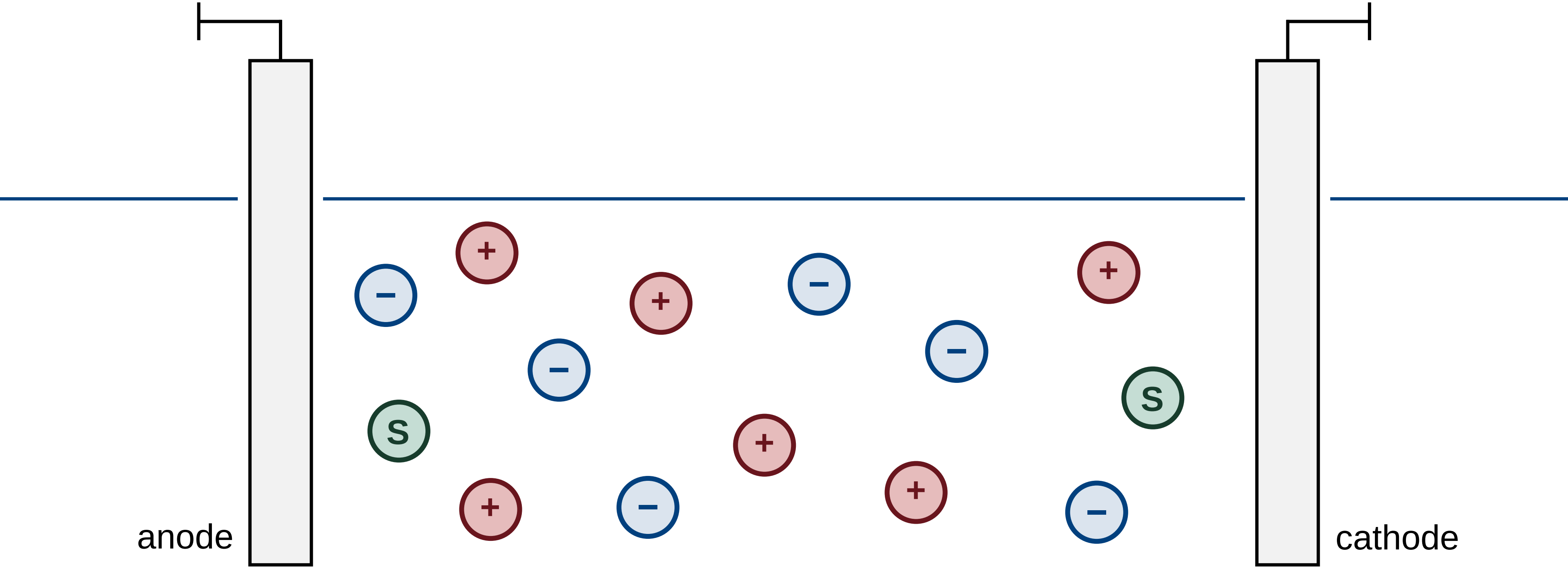


common sacrificial anodes:

zinc	magnesium
↓	↓
Ni catalysis	Alkyl–X, Si–X reduction

Potential of M^{2+} reduction determines the maximum cell potential possible when using a sacrificial anode

Electrolytes



common electrolytes:

$[A][PF_6]$ $[A][BF_4]$

$A = Li^+, Na^+, K^+, Cs^+, [NBu_4]^+$, etc.

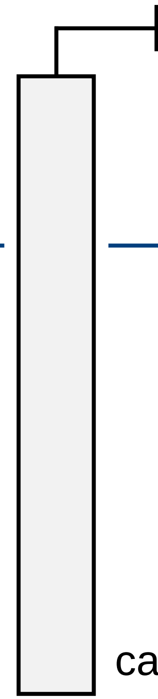
typical concentration > 0.1 M

practical concerns: cost and ease of separation from product

chemical concerns: affects cell resistance, maximum cell potential, and chemical environment at the electrode surface

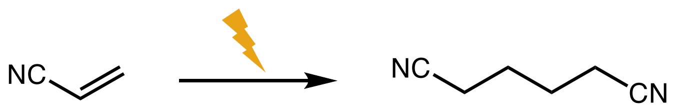
Kingston, C.; Baran, P. S.; et. al. Acc. Chem. Res. **2020**, 53, 72

Electrolytes



cathode

adiponitrile synthesis



common electrolytes:

$[A][PF_6]$ $[A][BF_4]$

A = Li^+, Na^+, K^+, Cs^+, $[NBu_4]^+$, etc.

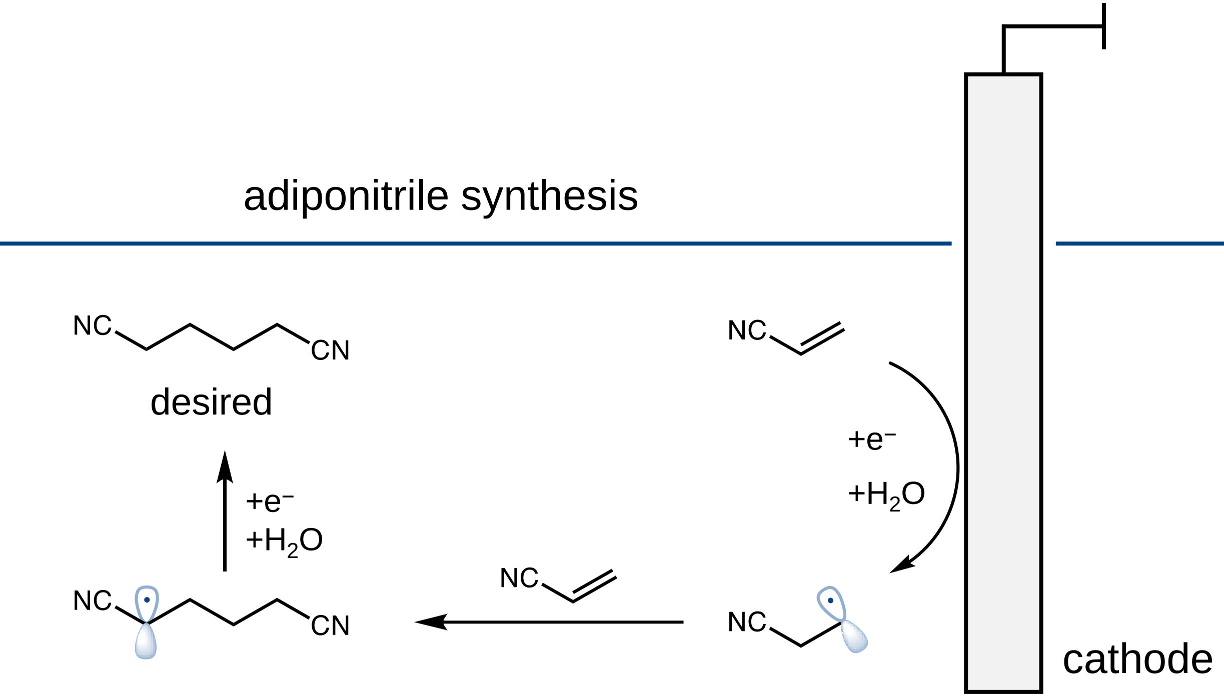
typical concentration > 0.1 M

practical concerns: cost and ease of separation from product

chemical concerns: affects cell resistance, maximum cell potential, and **chemical environment at the electrode surface**

Blanco, D. E.; Modestino, M. A.; et. al. J. Electrochem. Soc. **2020**, 167, 155526

Electrolytes



common electrolytes:

$[A][PF_6]$ $[A][BF_4]$

A = Li^+, Na^+, K^+, Cs^+, $[NBu_4]^+$, etc.

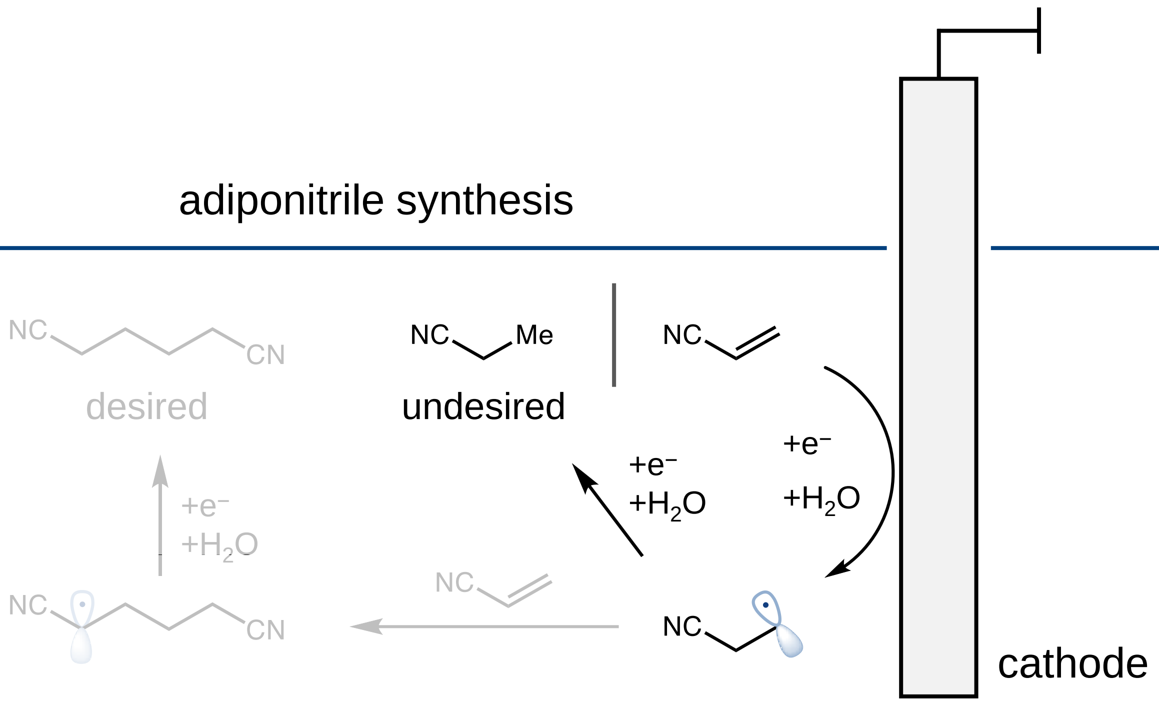
typical concentration > 0.1 M

practical concerns: cost and ease of separation from product

chemical concerns: affects cell resistance, maximum cell potential, and **chemical environment at the electrode surface**

Blanco, D. E.; Modestino, M. A.; et. al. J. Electrochem. Soc. **2020**, 167, 155526

Electrolytes



common electrolytes:

$[A][PF_6]$ $[A][BF_4]$

$A = Li^+, Na^+, K^+, Cs^+, [NBu_4]^+$, etc.

typical concentration > 0.1 M

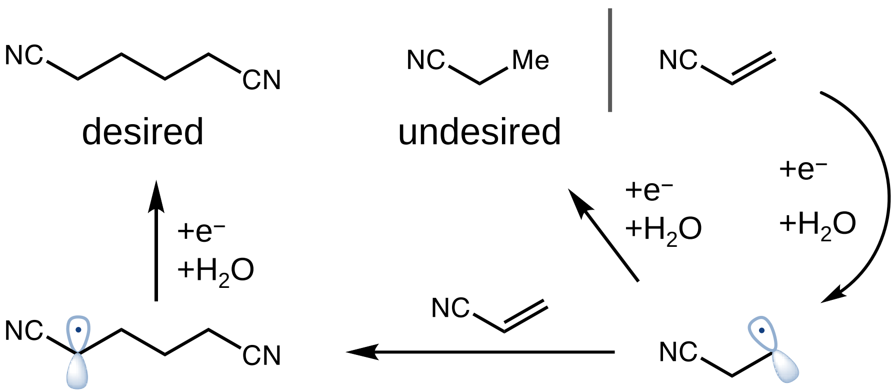
practical concerns: cost and ease of separation from product

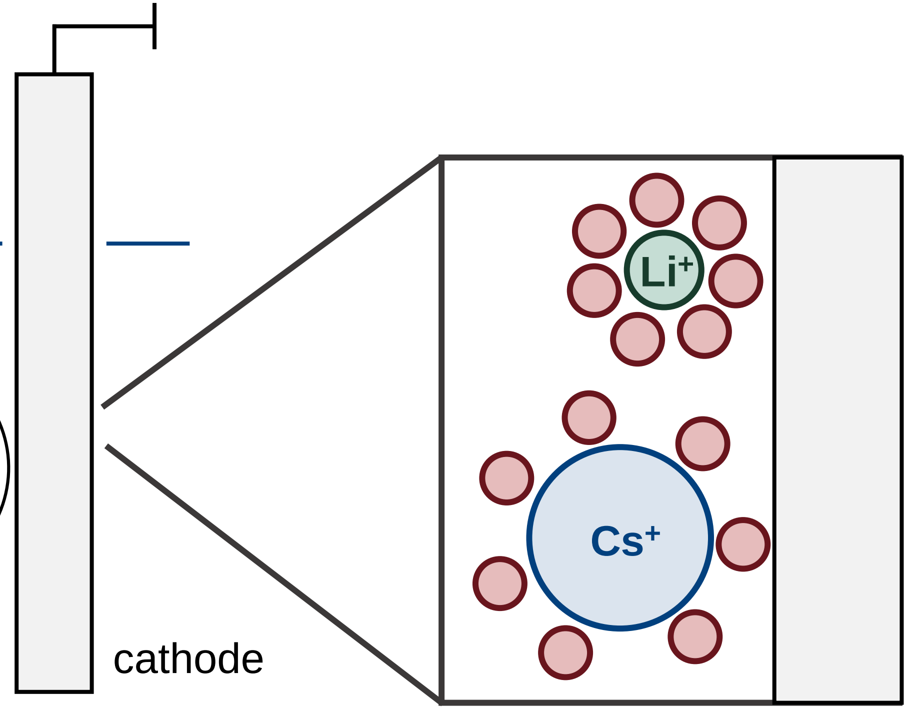
chemical concerns: affects cell resistance, maximum cell potential, and **chemical environment at the electrode surface**

Blanco, D. E.; Modestino, M. A.; et. al. J. Electrochem. Soc. **2020**, 167, 155526

Electrolytes

adiponitrile synthesis





common electrolytes:

[A][PF_6] [A][BF_4]

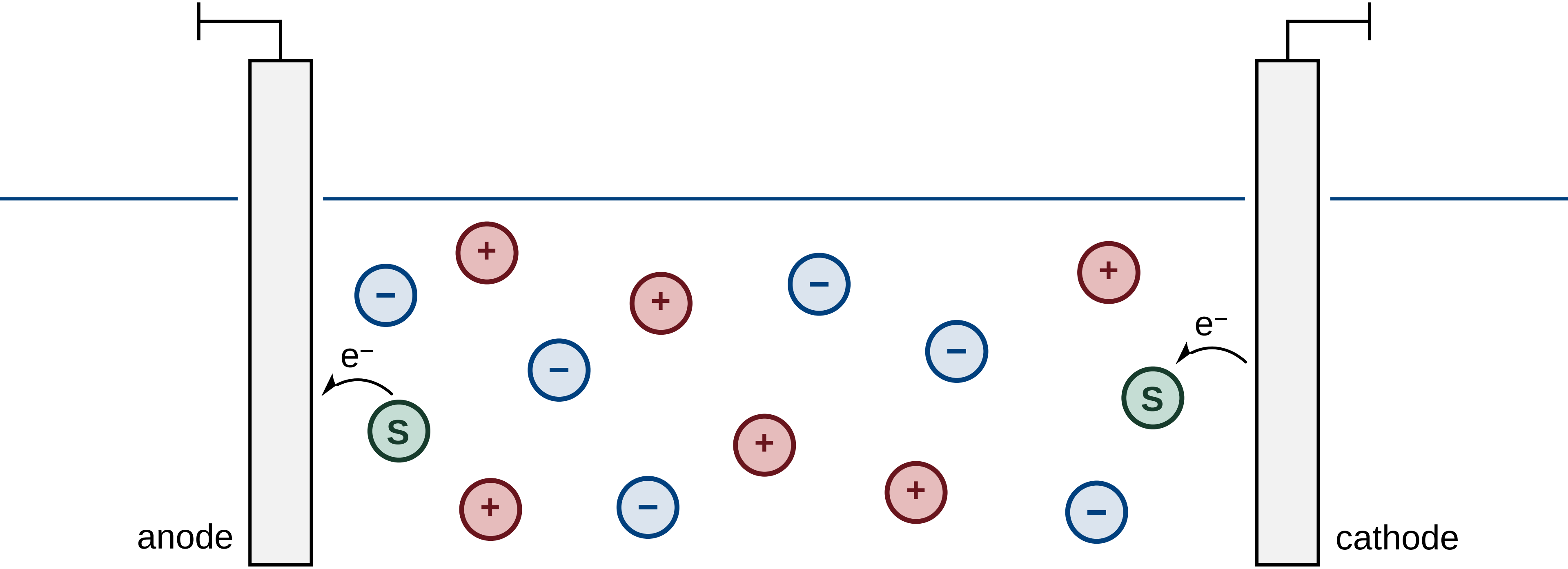
A = Li^+, Na^+, K^+, Cs^+, $[NBu_4]^+$, etc.

typical concentration > 0.1 M

alkali electrolyte with a larger hydration sphere minimizes H_2O near electrode, mitigating undesired over-reduction of acrylonitrile

Blanco, D. E.; Modestino, M. A.; et. al. J. Electrochem. Soc. **2020**, 167, 155526

Solvents



common solvents:

MeCN (ε = 38)

THF (ε = 7)

DMF (ε = 37)

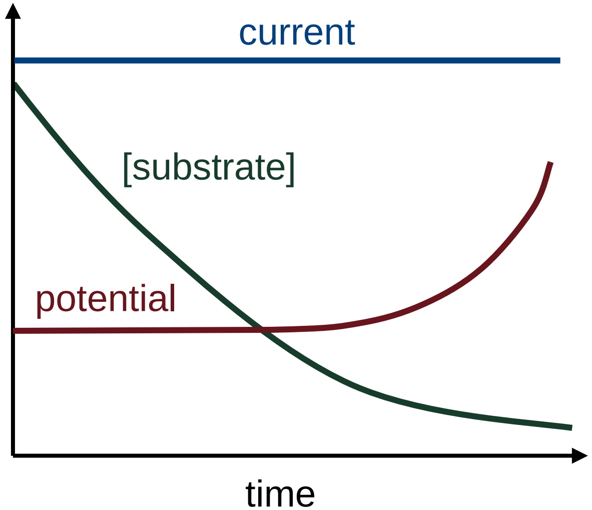
DMSO (ε = 47)

CH_2Cl_2 (ε = 9)

solvent must be sufficiently polar to allow electrolyte to ionize, and the solvent also typically sets the maximum cell potential

Methods for electrolysis

constant current
(galvanostatic)

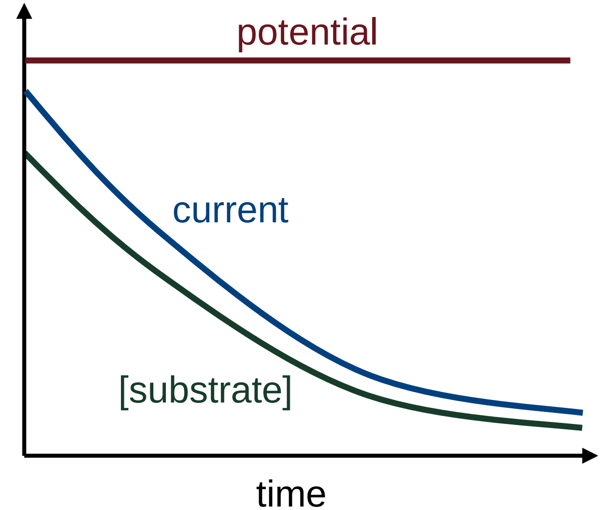


- ☐ *easiest option; don't need to know potential*
- ☐ can calculate charge passed/efficiency

$$\text{time (s)} = \frac{zNF}{I}$$

z = # of electrons
N = mol substrate
F = 96,485 s A mol^{-1}
I = current (A)

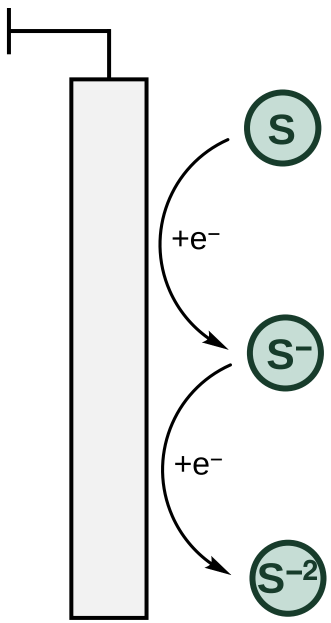
constant voltage
(potentiostatic)



- ☐ can be highly selective
- ☐ need to take CVs first; use 3-electrode setup
- ☐ difficult to determine charge passed/efficiency

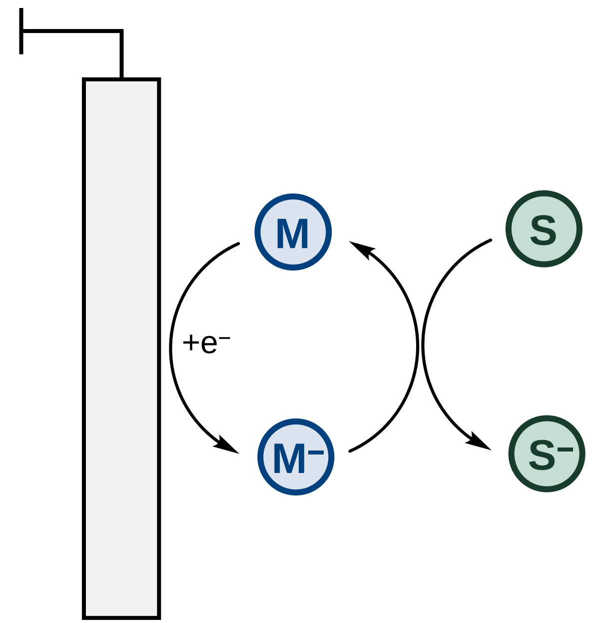
Methods for electrolysis

direct electrolysis



☐ often results in multiple, consecutive electron transfers from substrate to electrode

mediated electrolysis



☐ catalytic mediator can prevent over-oxidation or over-reduction of substrate

☐ appropriate mediator can be chosen based on CV studies

Electrochemistry equipment

standardized, reproducible

expensive ($2000-20,000)

not easy to modify or scale

ElectraSyn

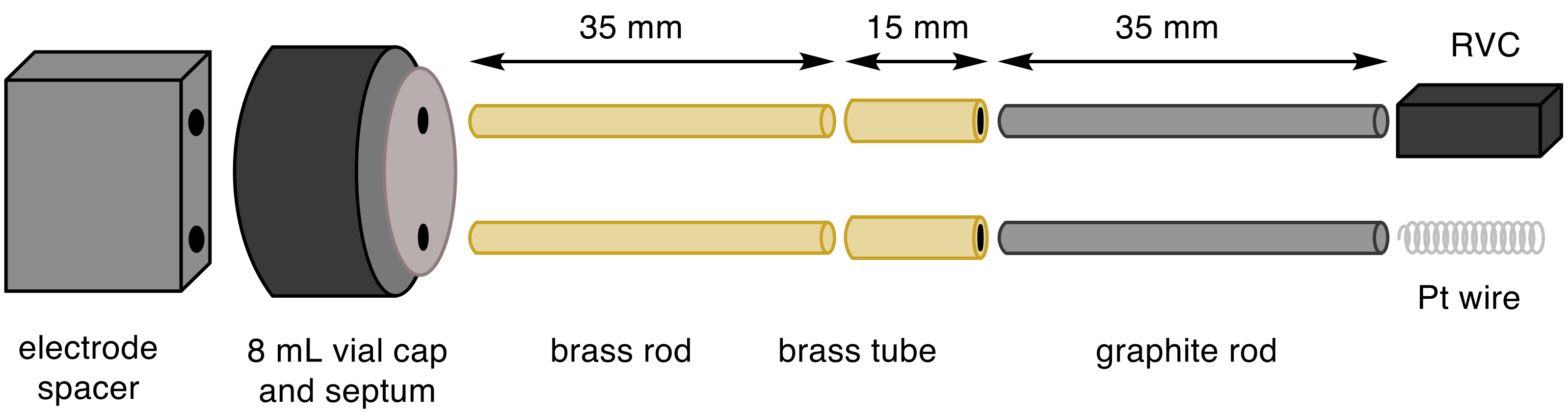
requires training and assembly

potential for irreproducibility

cheap ($200); modular, scalable

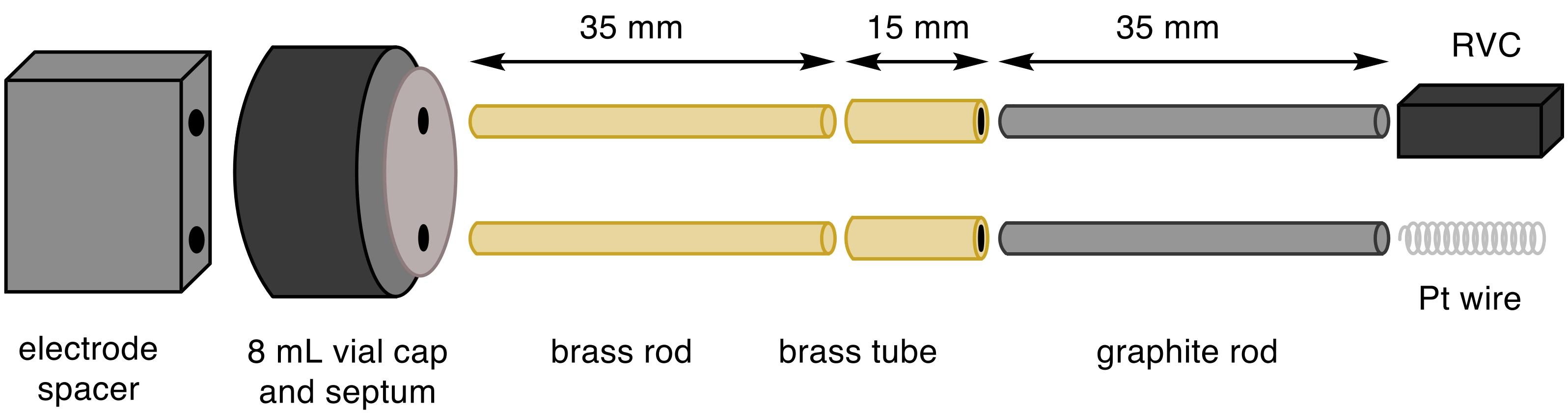
homebuilt

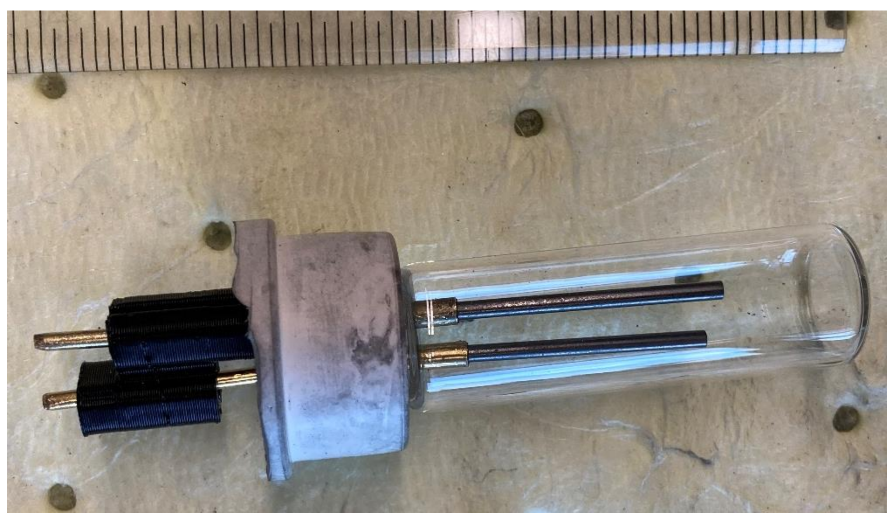
Electrochemistry equipment



apparatus based on: Fu, N.; Sauer, G. S.; Lin, S. Nat. Protoc. **2018**, 13, 1725

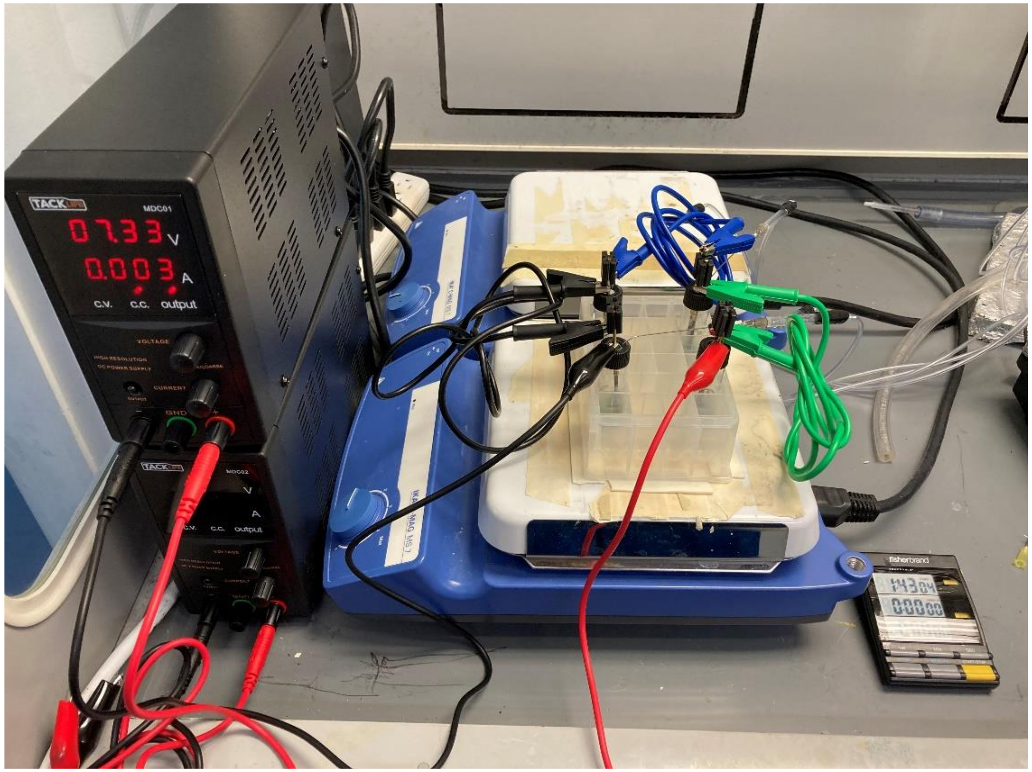
Electrochemistry equipment





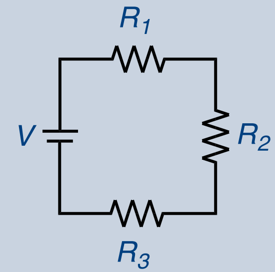
apparatus based on: Fu, N.; Sauer, G. S.; Lin, S. Nat. Protoc. **2018**, 13, 1725

Electrochemistry equipment



- 30 V, 5 A adjustable DC power supply
- 2 mm thick brass rod; 3mm OD/0.5 mm thick brass tube
- 2 mm pencil lead
- alligator clips

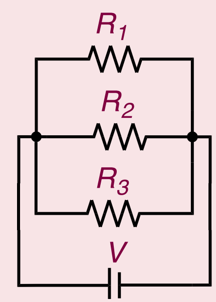
Series



$V = i\,(R_1 + R_2 + R_3)$

i = constant

Parallel

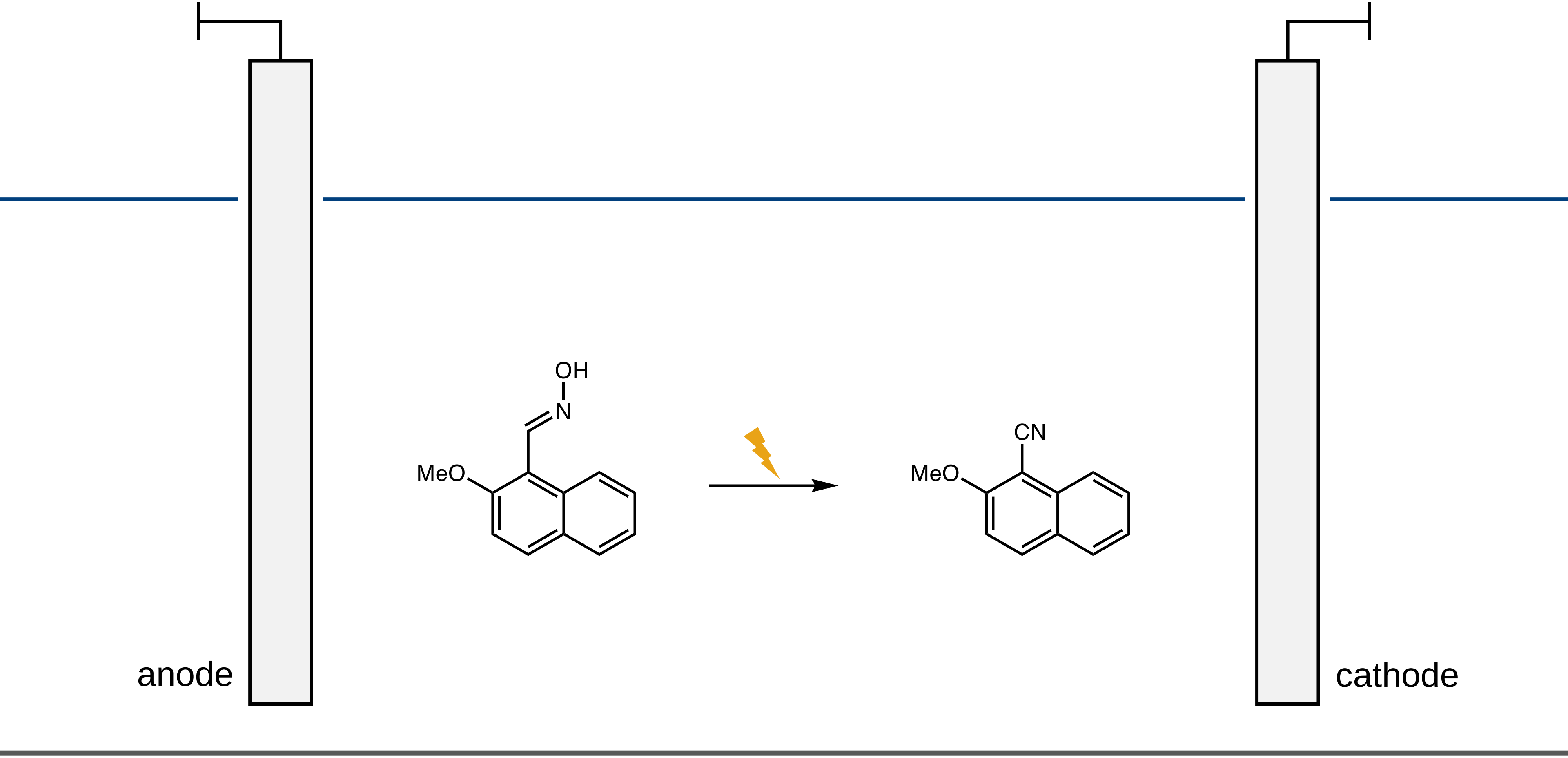


$i = V\,/\,(R_1 + R_2 + R_3)$

V = constant

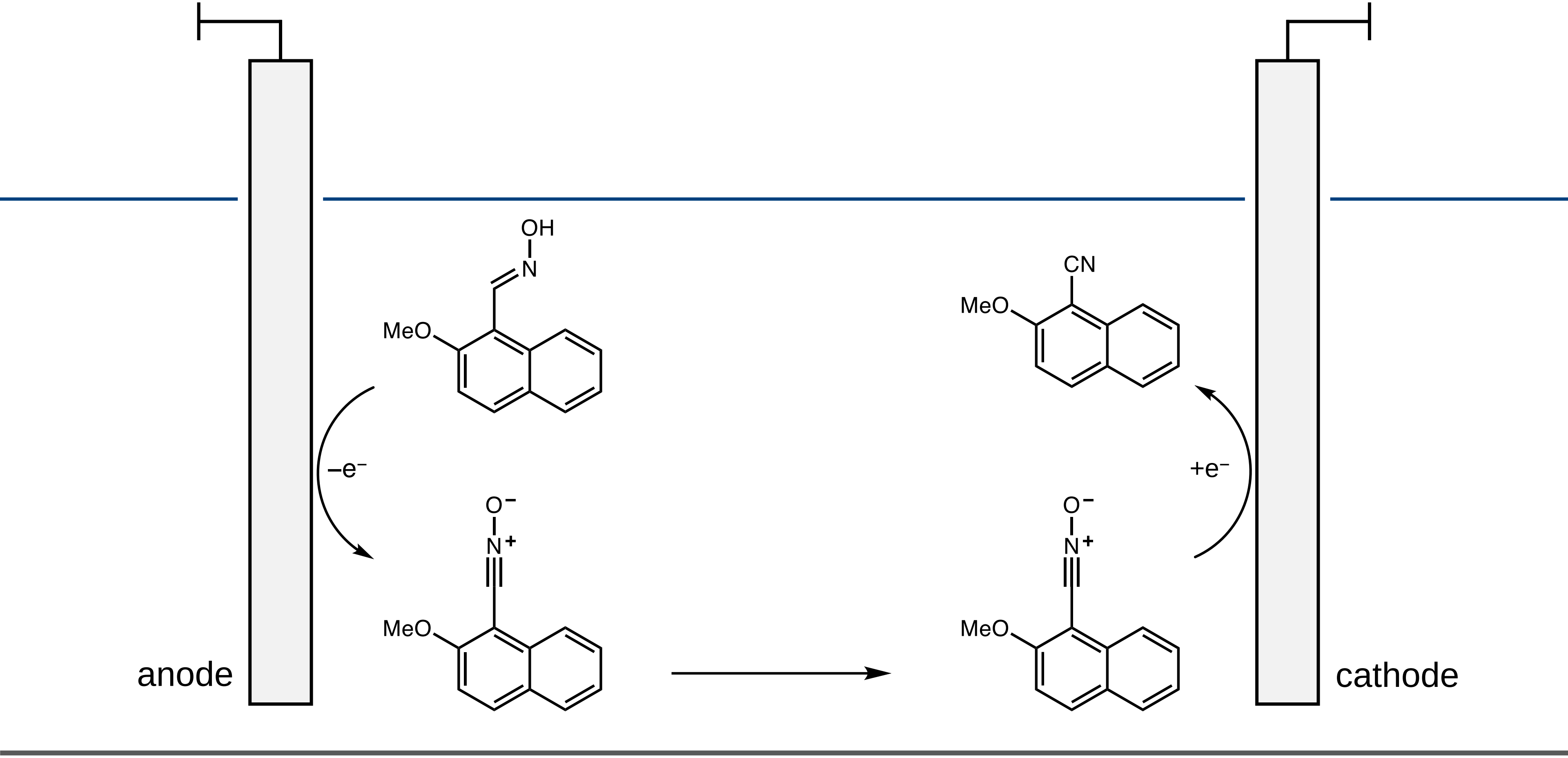
apparatus based on: Fu, N.; Sauer, G. S.; Lin, S. Nat. Protoc. **2018**, 13, 1725

Designing an electrochemical reaction



Hartmer, M. F.; Waldvogel, S. R. Chem. Commun. **2015**, 51, 16346

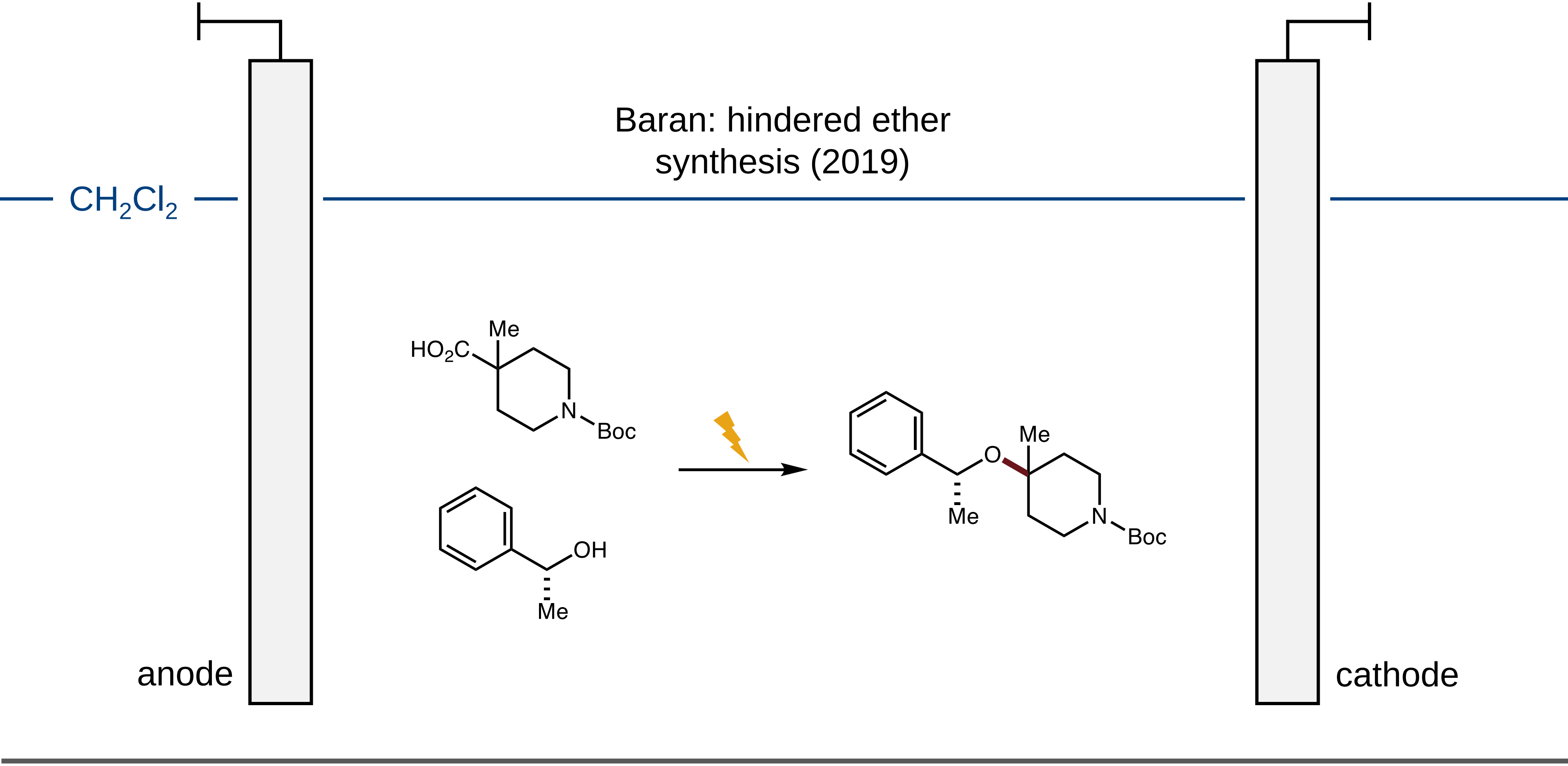
Designing an electrochemical reaction



#1: The vast majority of reactions occur at a single electrode; for reactions where species cross between electrodes, intermediates must be persistent

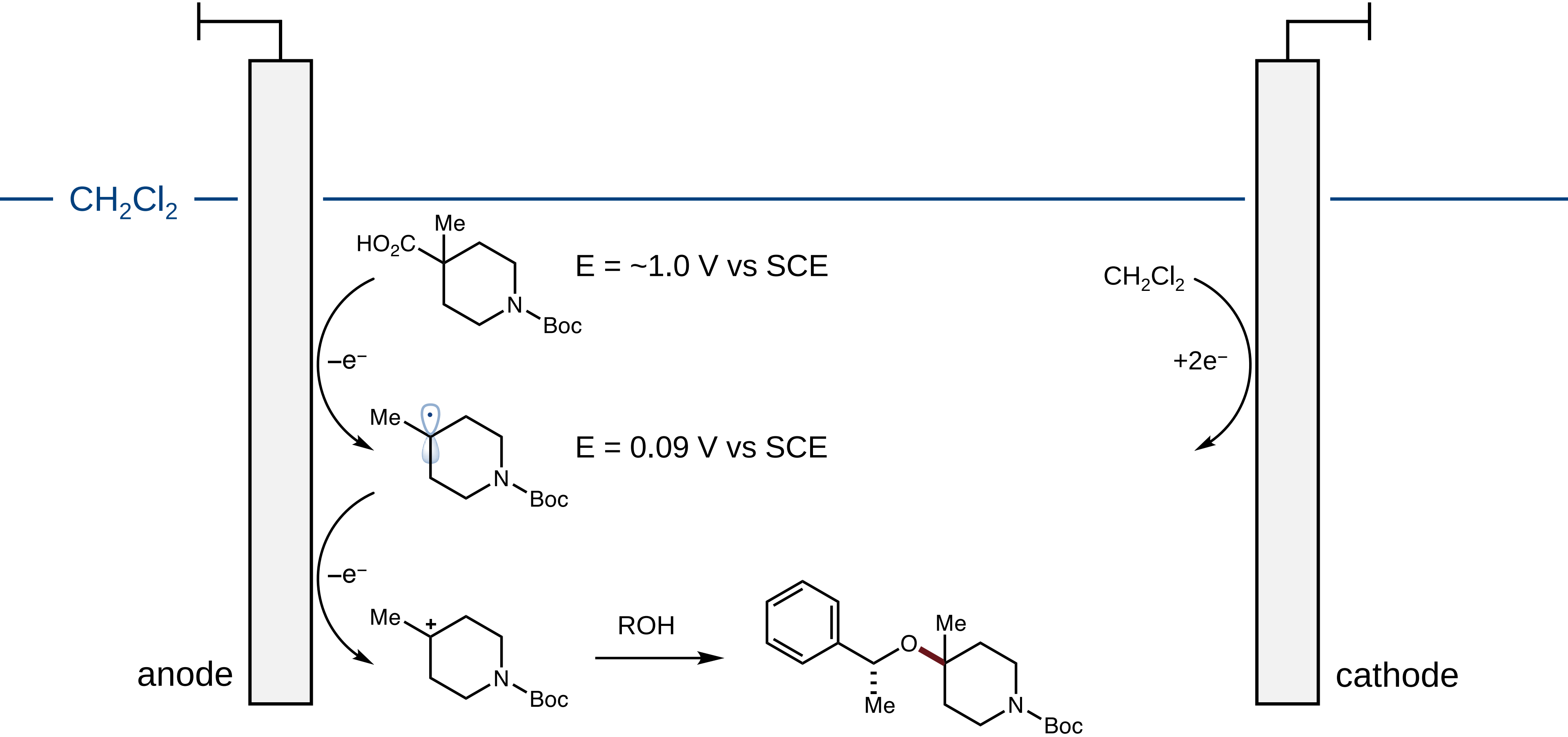
Hartmer, M. F.; Waldvogel, S. R. Chem. Commun. **2015**, 51, 16346

Designing an electrochemical reaction



Xiang, J.; Shang, M.; Baran, P. S.; et. al. Nature **2019**, 573, 398

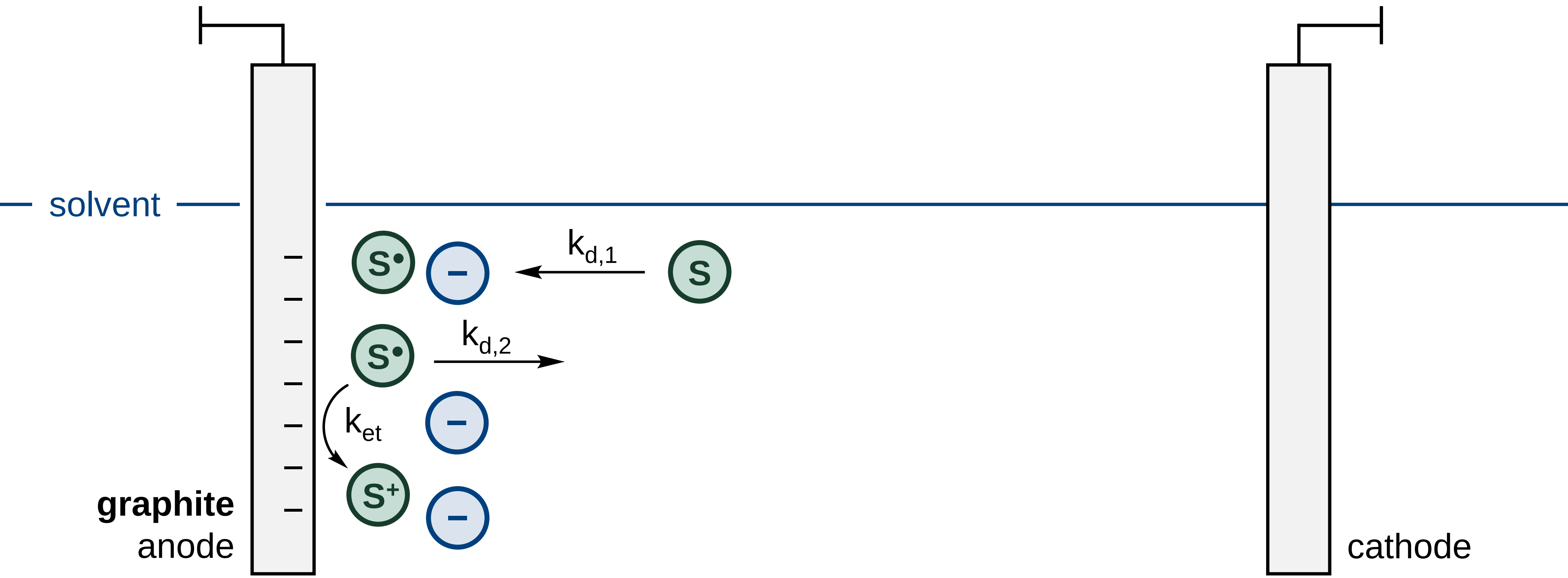
Designing an electrochemical reaction



#2: Often, electrochemical reactions have a domino-like mechanism, where substrate oxidation leads to a more easily-oxidized intermediate and so on, until an electrochemically-stable product is formed

Wayner, D. D. M.; et. al. Am. Chem. Soc. **1988**, 110, 132

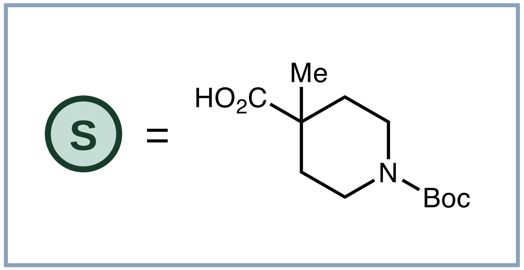
Favoring sequential oxidation processes



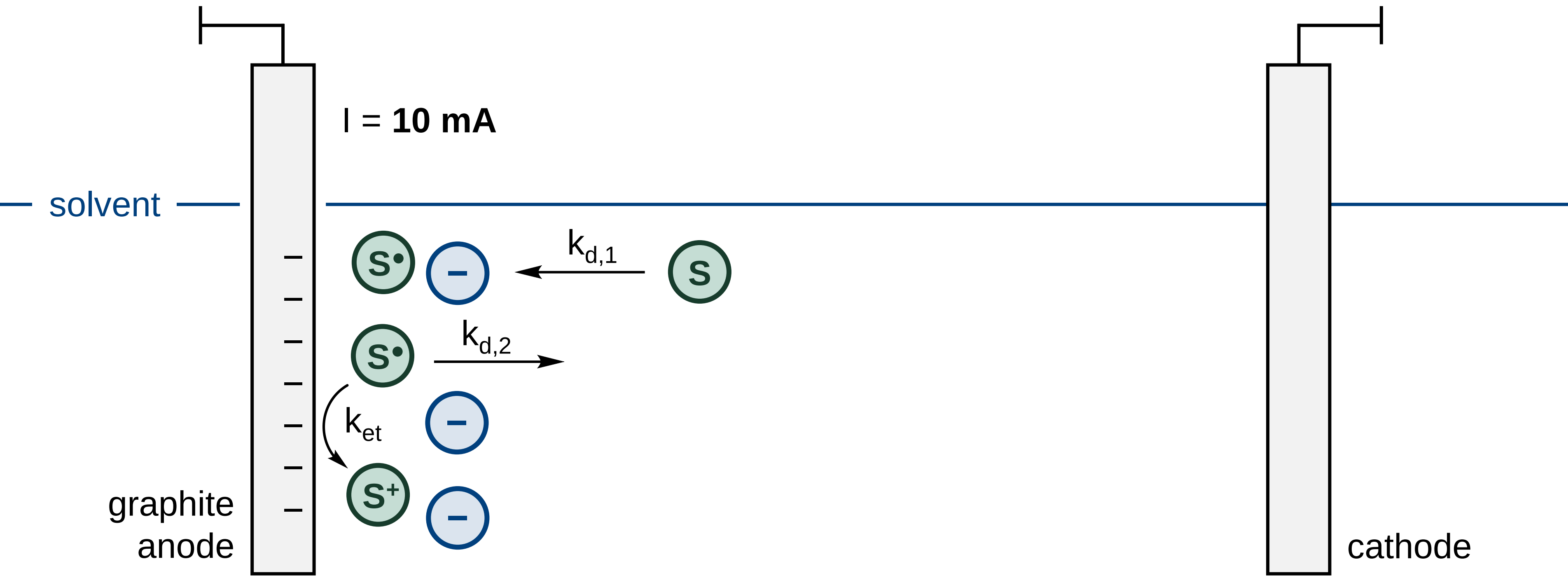
product formation is favored when electron transfer is faster than diffusion

↓

graphite anode adsorbs radicals, slowing diffusion away from electrode

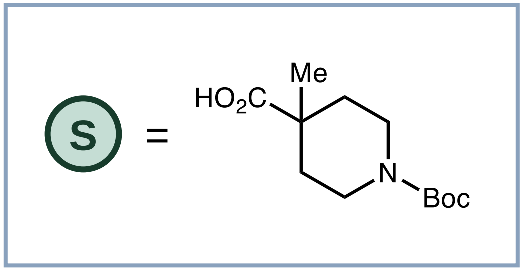


Favoring sequential oxidation processes



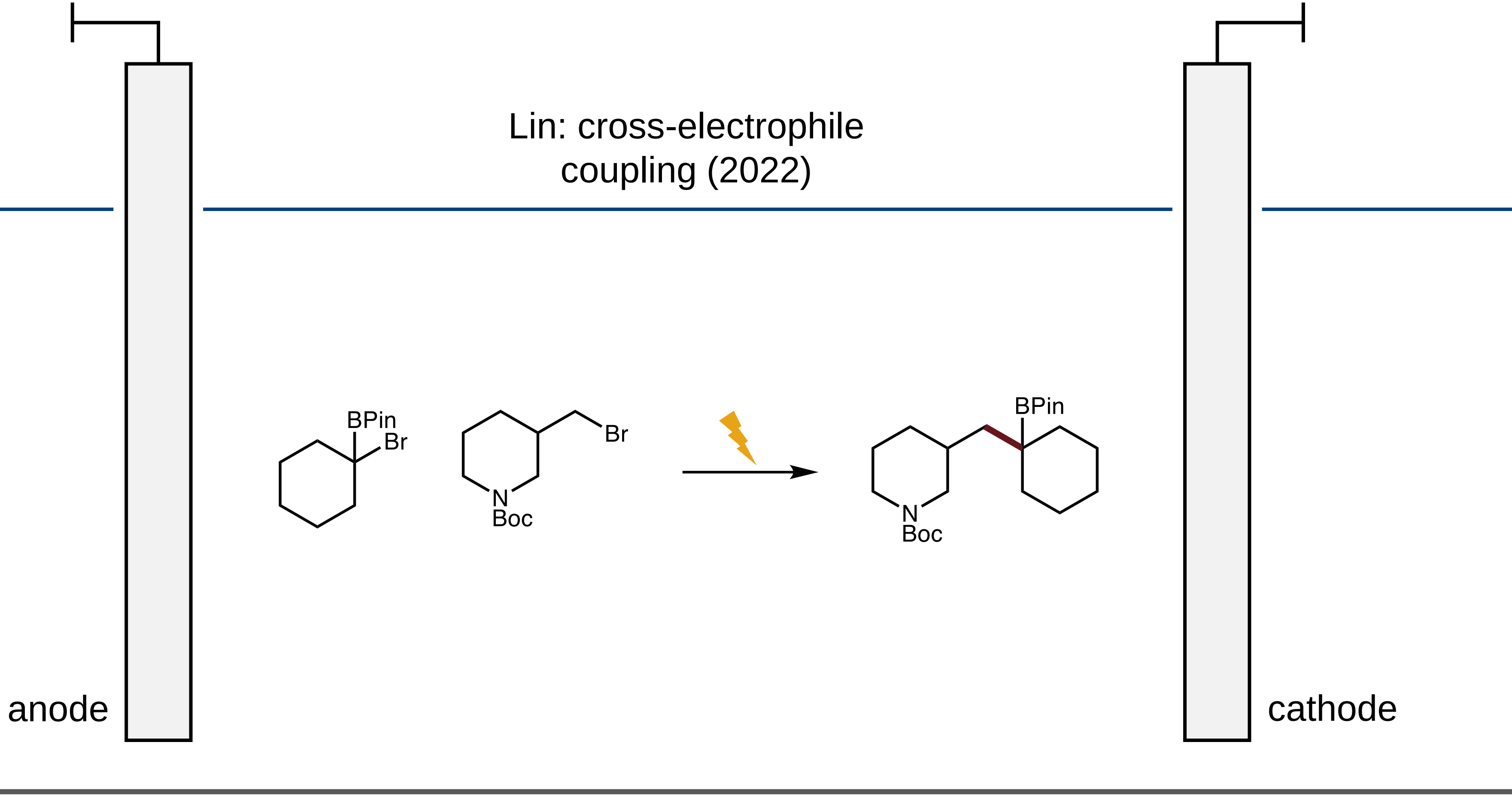
product formation is favored when electron transfer is faster than diffusion

high current increases the rate of electron transfer at the anode surface



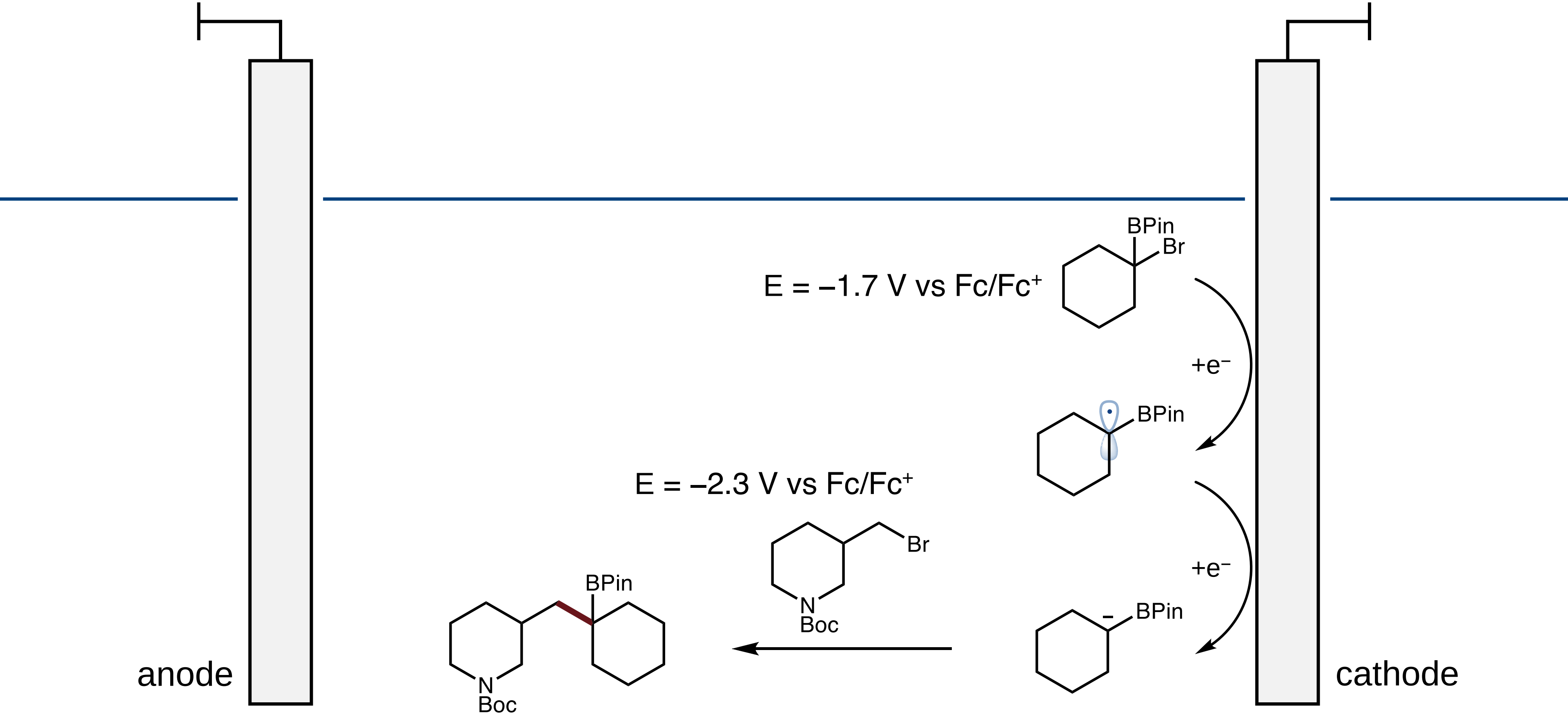
Designing an electrochemical reaction

Lin: cross-electrophile coupling (2022)



Zhang, W.; See, K. A.; Lin, S.; et. al. Nature **2022**, 604, 292

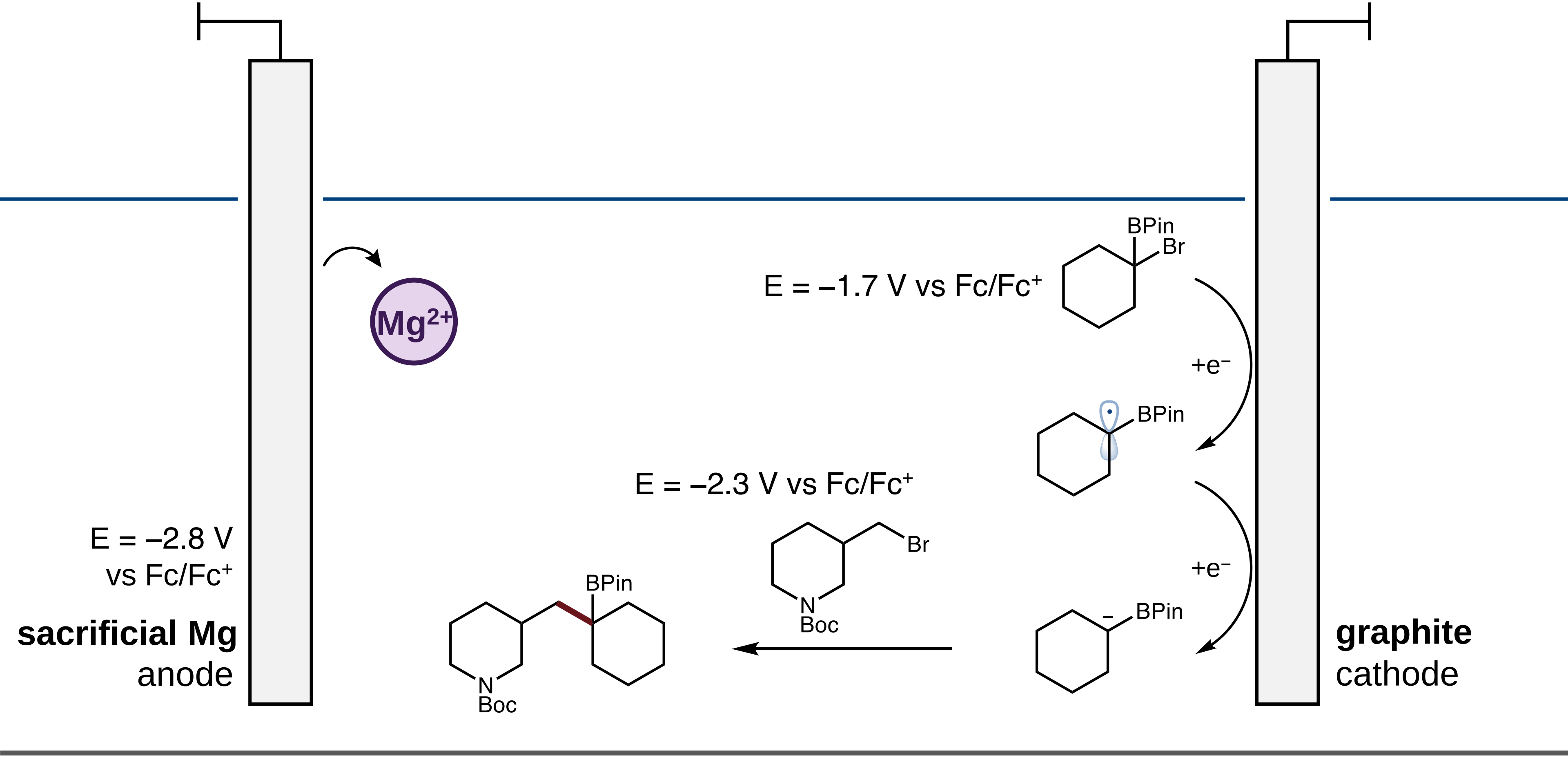
Designing an electrochemical reaction



#2: Often, electrochemical reactions have a domino-like mechanism, where substrate reduction leads to a more easily-reduced intermediate and so on, until an electrochemically-stable product is formed

Zhang, W.; See, K. A.; Lin, S.; et. al. Nature **2022**, 604, 292

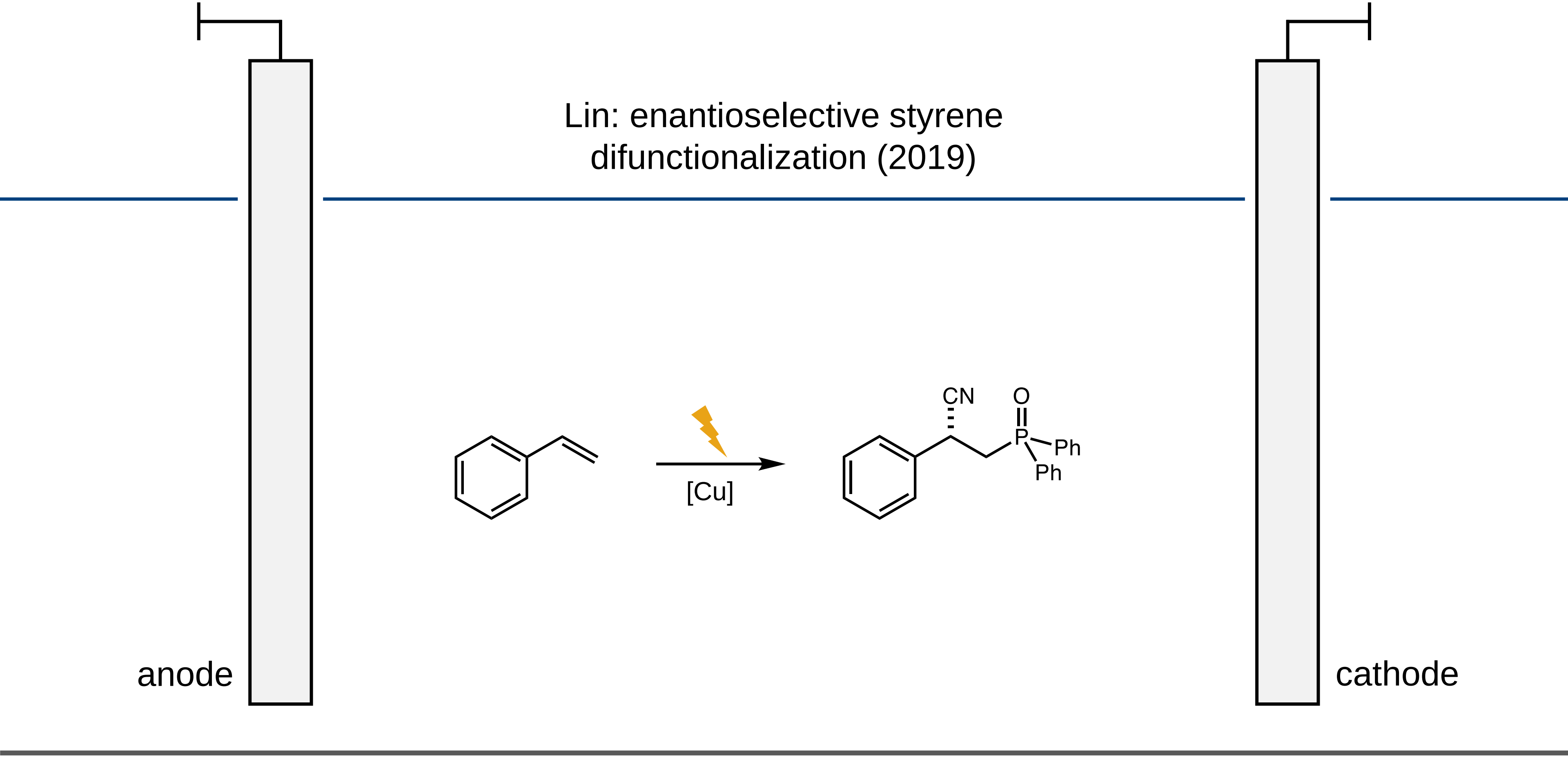
Promoting sequential reduction of substrate



Zhang, W.; See, K. A.; Lin, S.; et. al. Nature **2022**, 604, 292

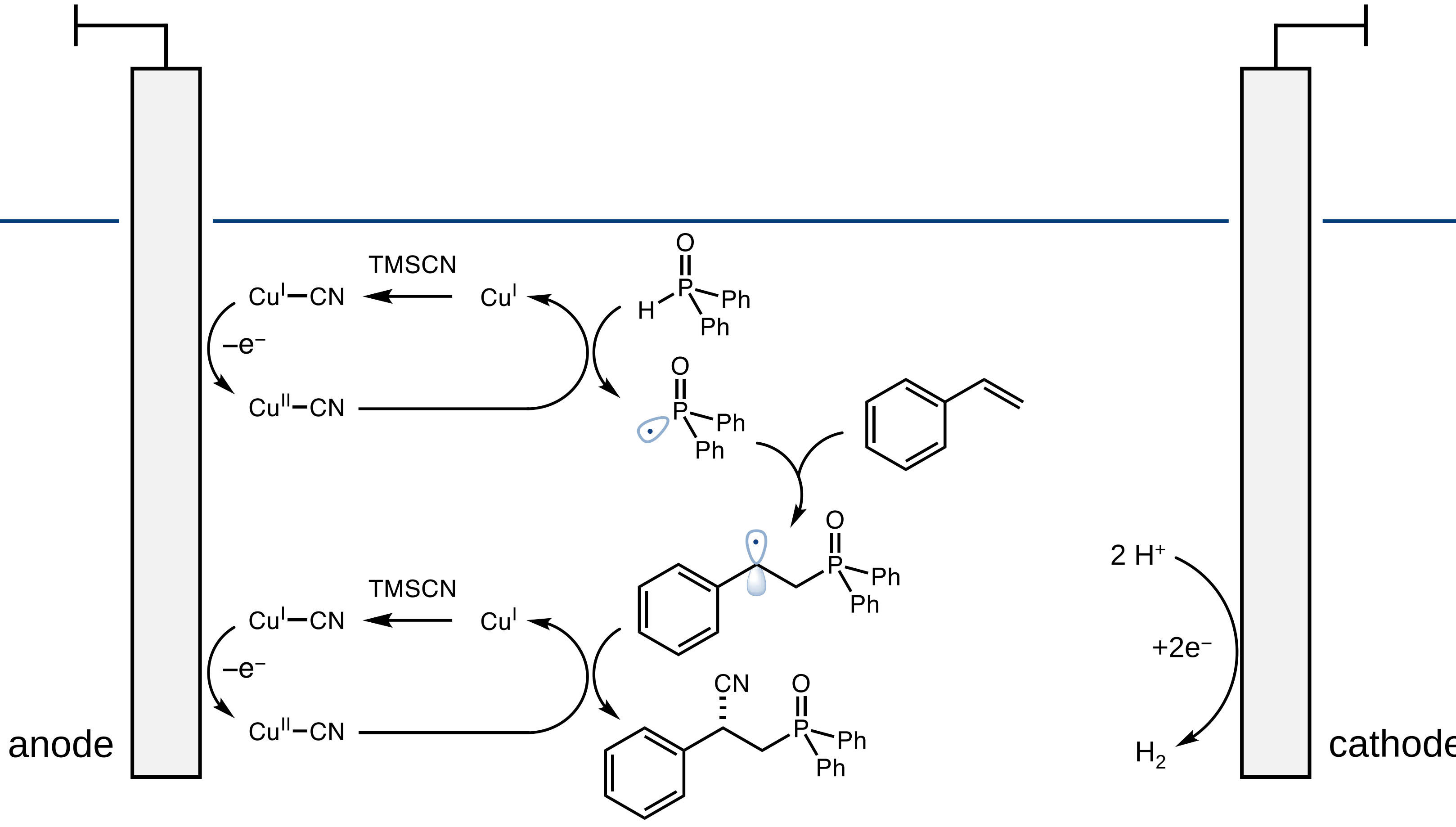
Designing an electrochemical reaction

Lin: enantioselective styrene difunctionalization (2019)



Fu, N.; Song, L.; Lin, S.; et. al. J. Am. Chem. Soc. **2019**, 141, 14480

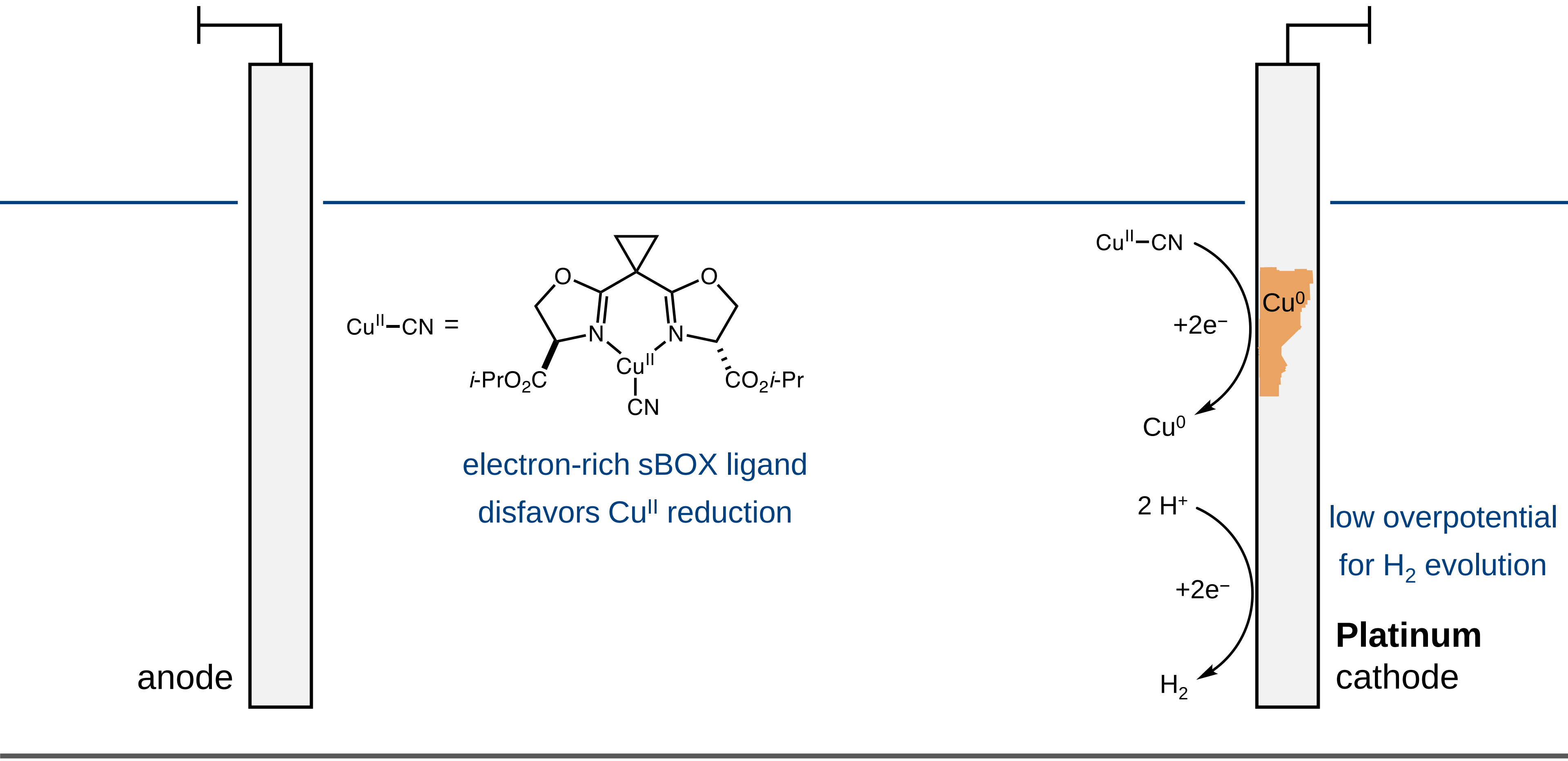
Designing an electrochemical reaction



#3: The reaction occurring at the counter electrode can be as important to consider as the desired reaction

Fu, N.; Song, L.; Lin, S.; et. al. J. Am. Chem. Soc. **2019**, 141, 14480

Favoring proton reduction over copper plating



Fu, N.; Song, L.; Lin, S.; et. al. J. Am. Chem. Soc. **2019**, 141, 14480

Designing an electrochemical reaction

#1: The vast majority of reactions occur at a single electrode; for reactions where species cross between electrodes, intermediates must be persistent

#2: Often, electrochemical reactions have a domino-like mechanism, where substrate reduction leads to a more easily-reduced intermediate and so on, until an electrochemically-stable product is formed

#3: The reaction occurring at the counter electrode can be as important to consider as the desired reaction

Questions?