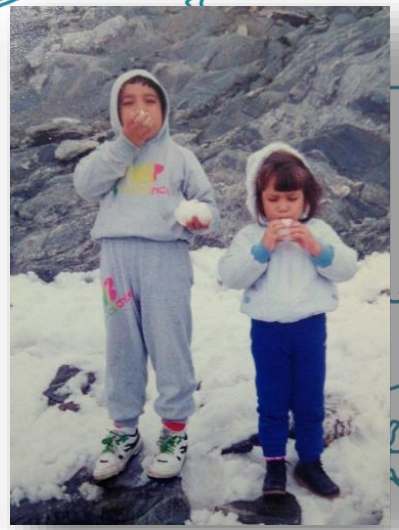
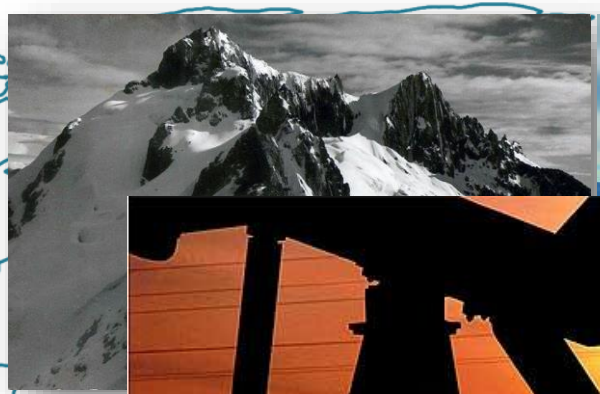
Engineering Electrochemical Manufacturing: From High-Performing Reactors to Separation Processes

Miguel A. Modestino
Dept. of Chemical and Biomolecular Engineering
Tandon School of Engineering, New York University

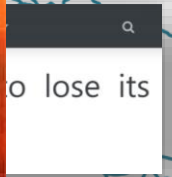
NYU

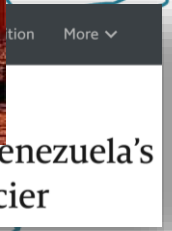
A short story about myself



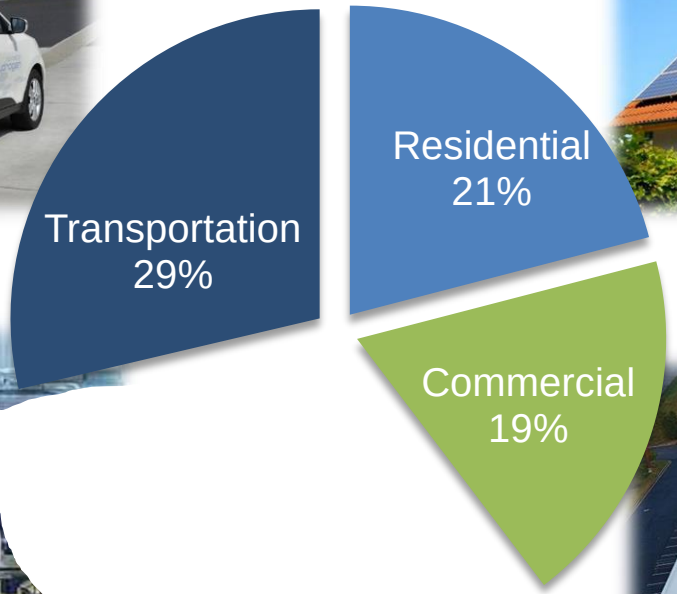


Venezuela
1985 - 2003





Solar in sectors that SUFFER from INTERMITTENCY



Chemical Industry by Sectors

Basic Chemicals:
organic and inorganic chemicals, plastic, dyes.

Specialty Chemicals:
adhesives, additives, catalysts and coatings.

Agricultural Chemicals:
Chemicals for farm economy and the food processing.

Pharmaceuticals:
drugs, vaccines, vitamins, for human and veterinary.

Consumer Products:
detergents, and cleaners, cosmetics.

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Case Study: Petroleum Derived Chemicals

Refining

Gasoline
Diesel
Jet Fuel
Oil Gasses
Petrochemical Feedstocks

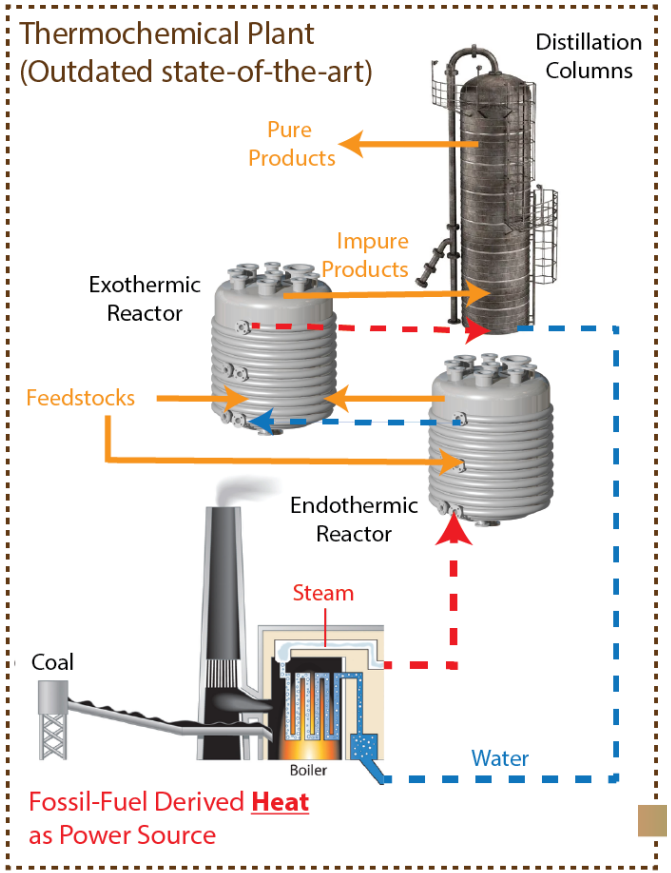
Petrochemicals

Polymers
Intermediates
Additives

Oil companies expecting to go from **5-20%** to **40-50%** of output petrochemical starting 2025

Tullo, A. Why the future of oils is in chemicals, not fuels. Chemical & Engineering News. Volume 97, Issue 8, 2019.

Approaches to Electrification of Chemical Manufacturing

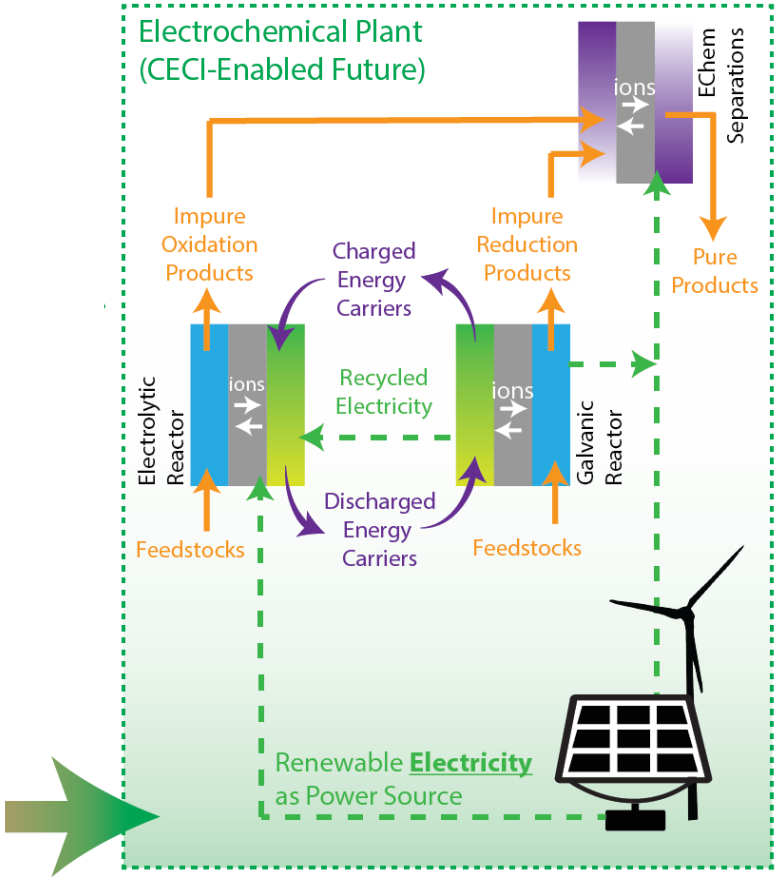


Approaches to Electrification of Chemical Manufacturing

Separations:
Distillations
↓
Membranes/Electrochemical Separations

Reactions:
Thermochemical
↓
Electrochemical

Energy Recycling:
Heat/Steam
↓
Chemical Potential



Role of Electrochemical Separations

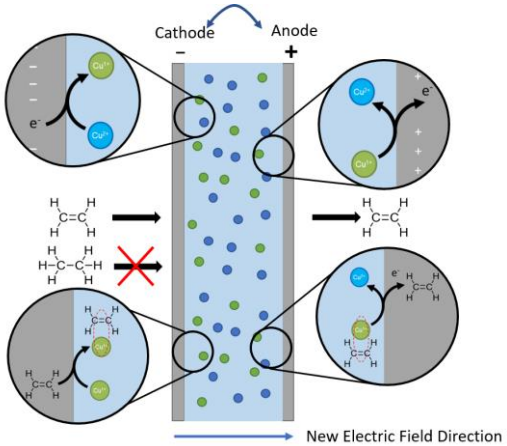
Significance of separations in chemical manufacturing

- 10-15% of US Energy Consumption
- Oil Refining major contributor
  - >200 million tons of ethylene/propylene (30 kg/person)
- Olefin/Paraffin separation by cryogenic distillation

Sholl, Lively, Nature, **532,** 435–437

Electrochemical Approach to Olefin Separations

Olefins



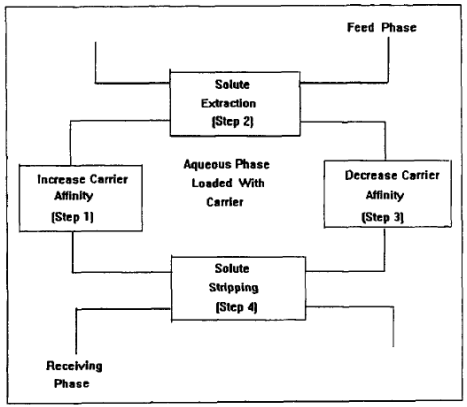
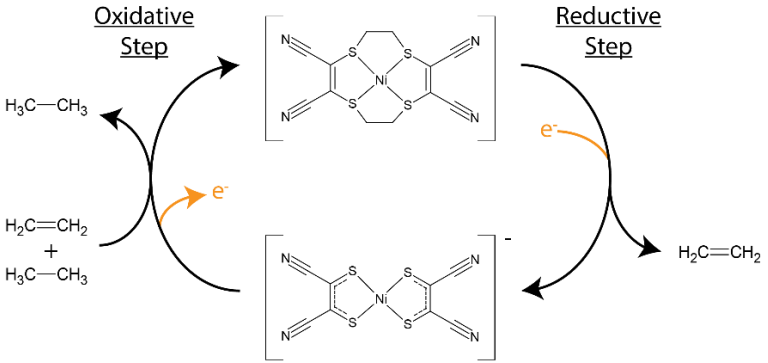


Figure 1. Continuous electrochemically modulated complexation process.

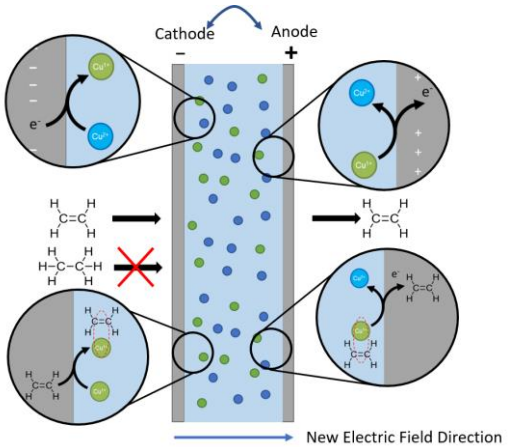


Suzuki, Noble, Koval, Inorg. Chem. 1997, 36, 136
Terry et al. (1997). J. AIChE, 7, 43, 1709

Wang, Stiefel. (2001). Science, 291, 106

Electrochemical Approach Impact Other Separations

Olefins



Wang, Stiefel. (2001). Science, 291, 106

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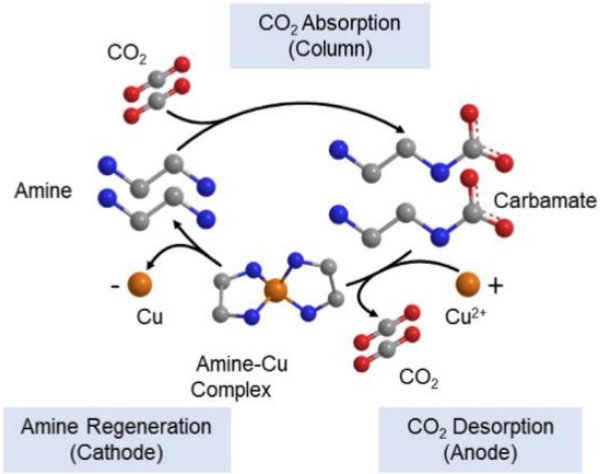
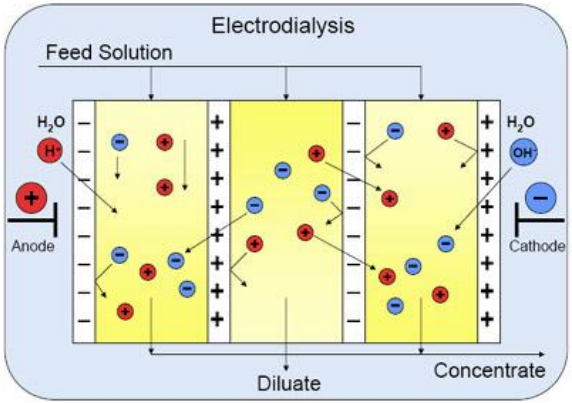
CO_2 capture



Wang, Miao, et al. *Applied Energy* 255 (2019): 113879.

Gurkan, Simeon, and Hatton, ACS Sustainable Chemistry & Engineering, (2015), 3 (7), pp 1394–1405.

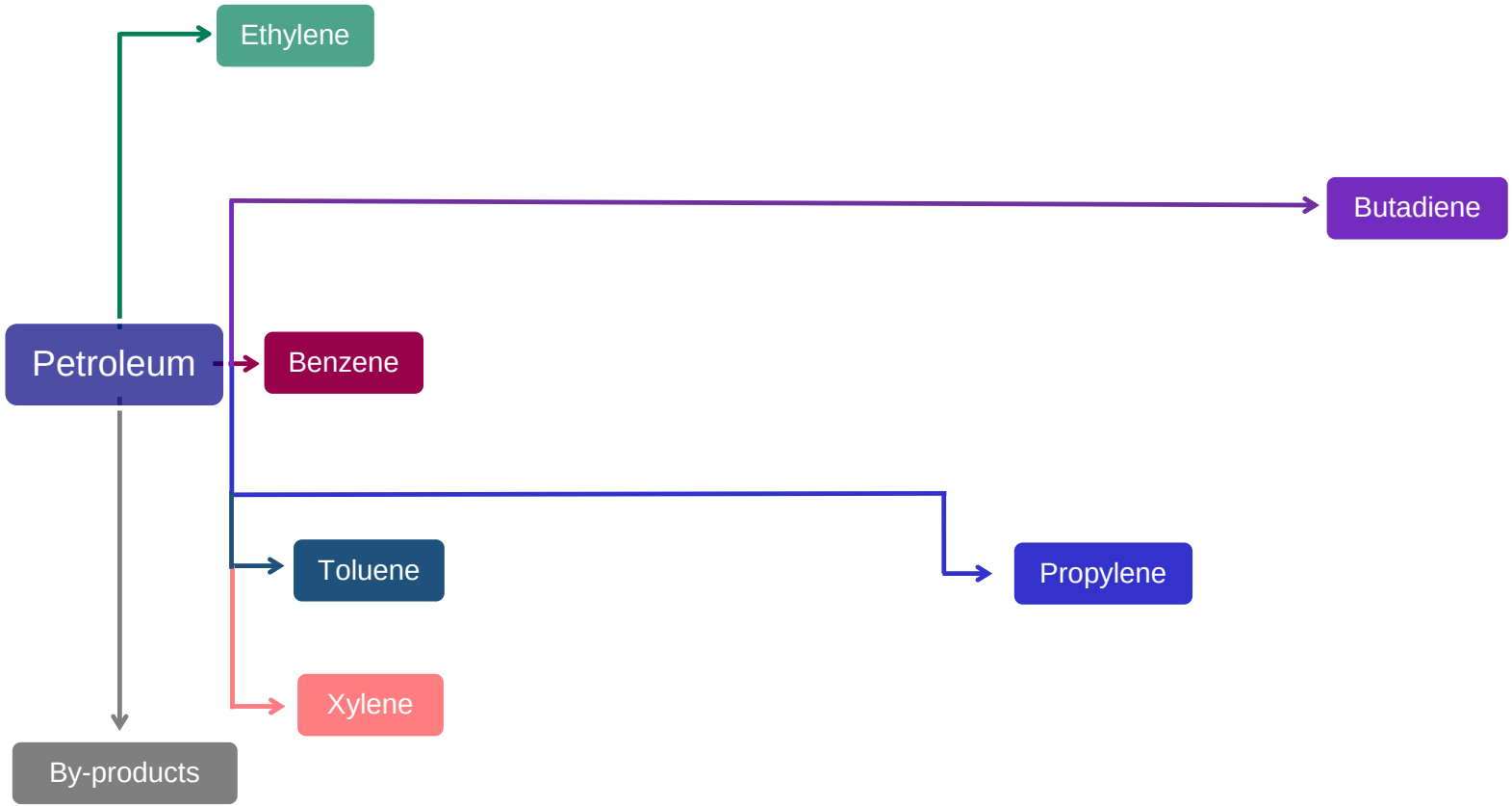
Water Purification



https://www.fumatech.com/EN/Membrane processes/Process%2Bdescription/Electrodialysis/index.html

How about Reaction Processes?

Industrial Petrochemical Processes



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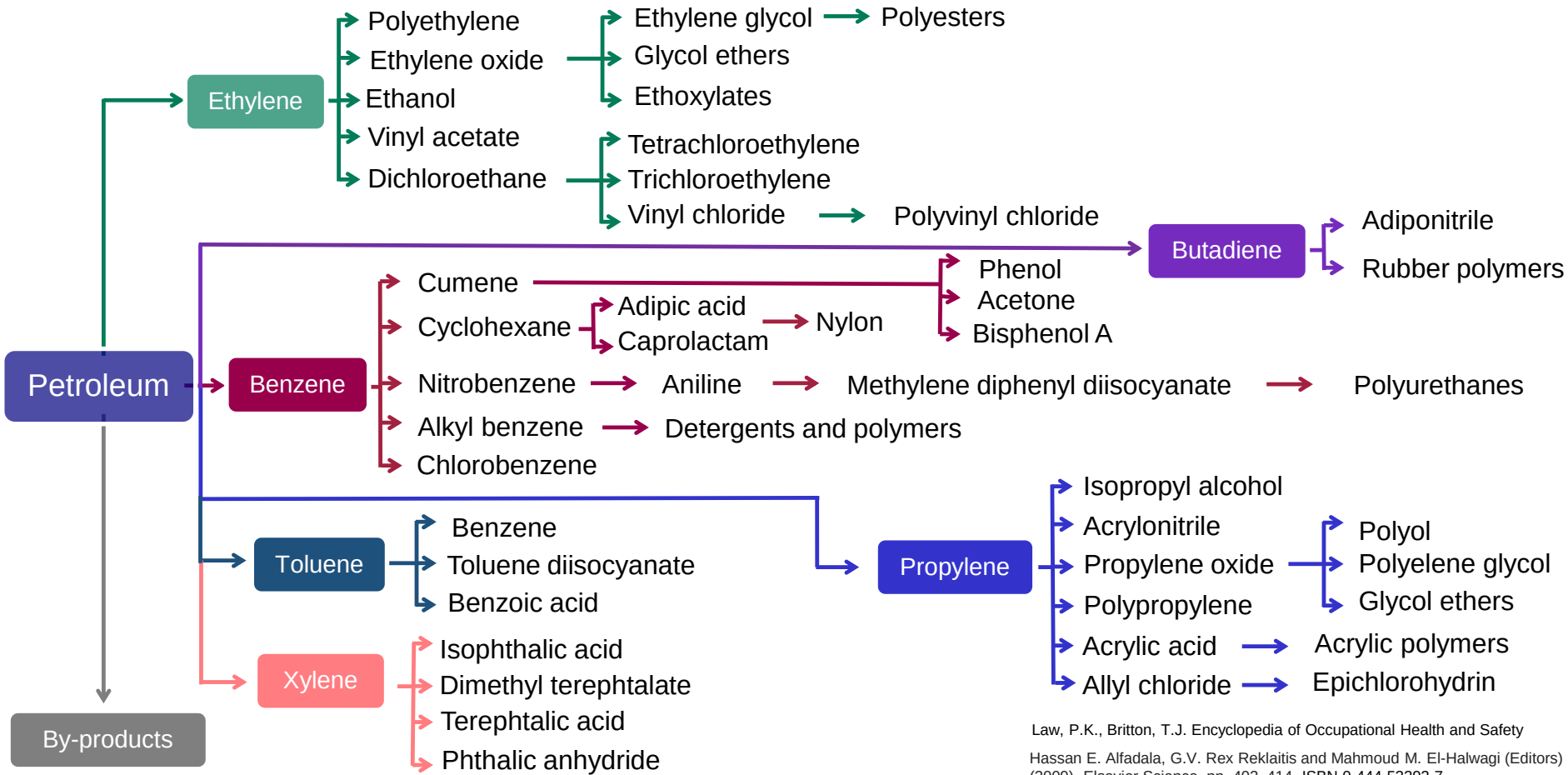

Law, P.K., Britton, T.J. Encyclopedia of Occupational Health and Safety

Hassan E. Alfadala, G.V. Rex Reklaitis and Mahmoud M. El-Halwagi (Editors) (2009). Elsevier Science. pp. 402–414. ISBN 0-444-53292-7.

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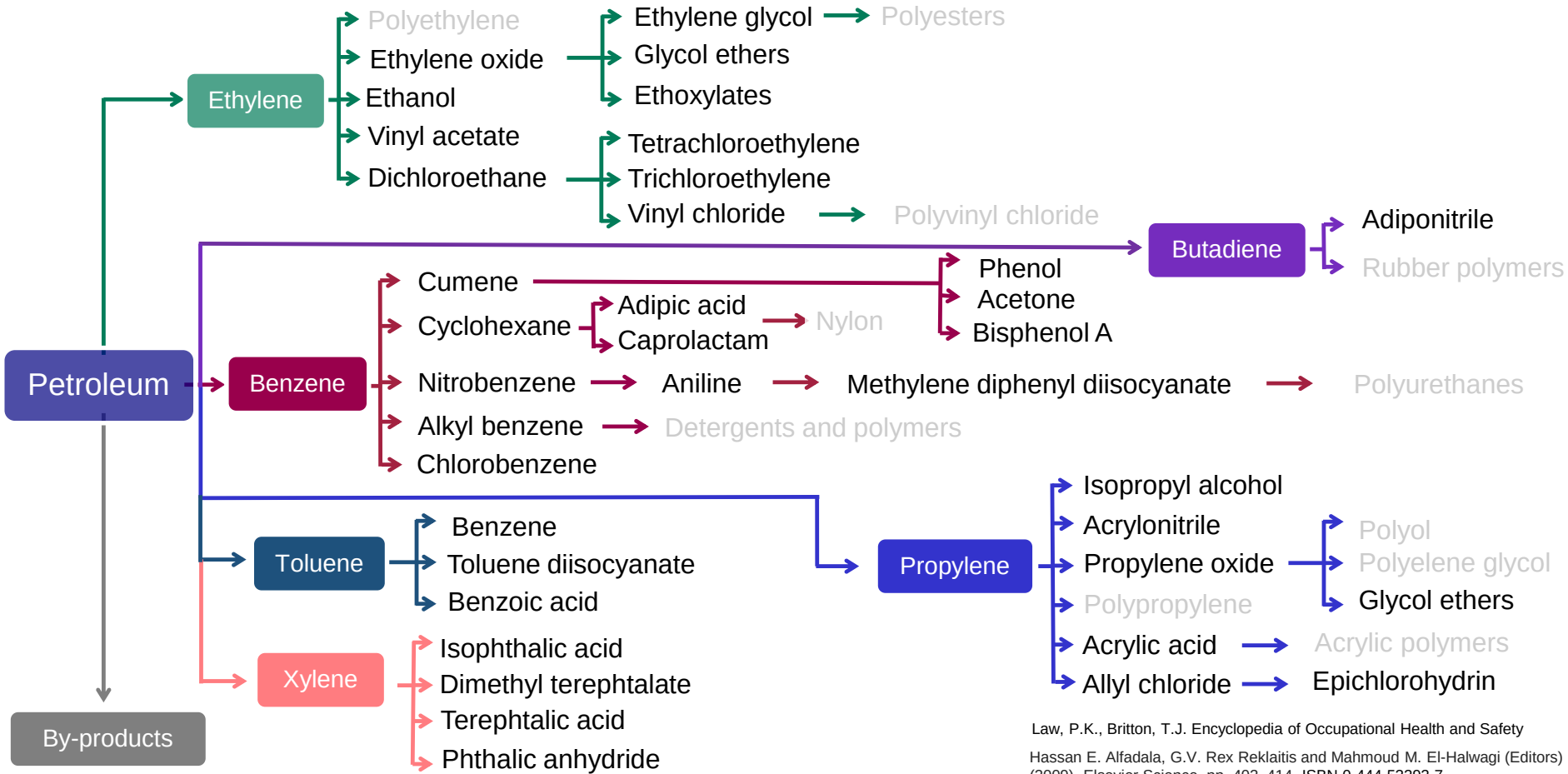

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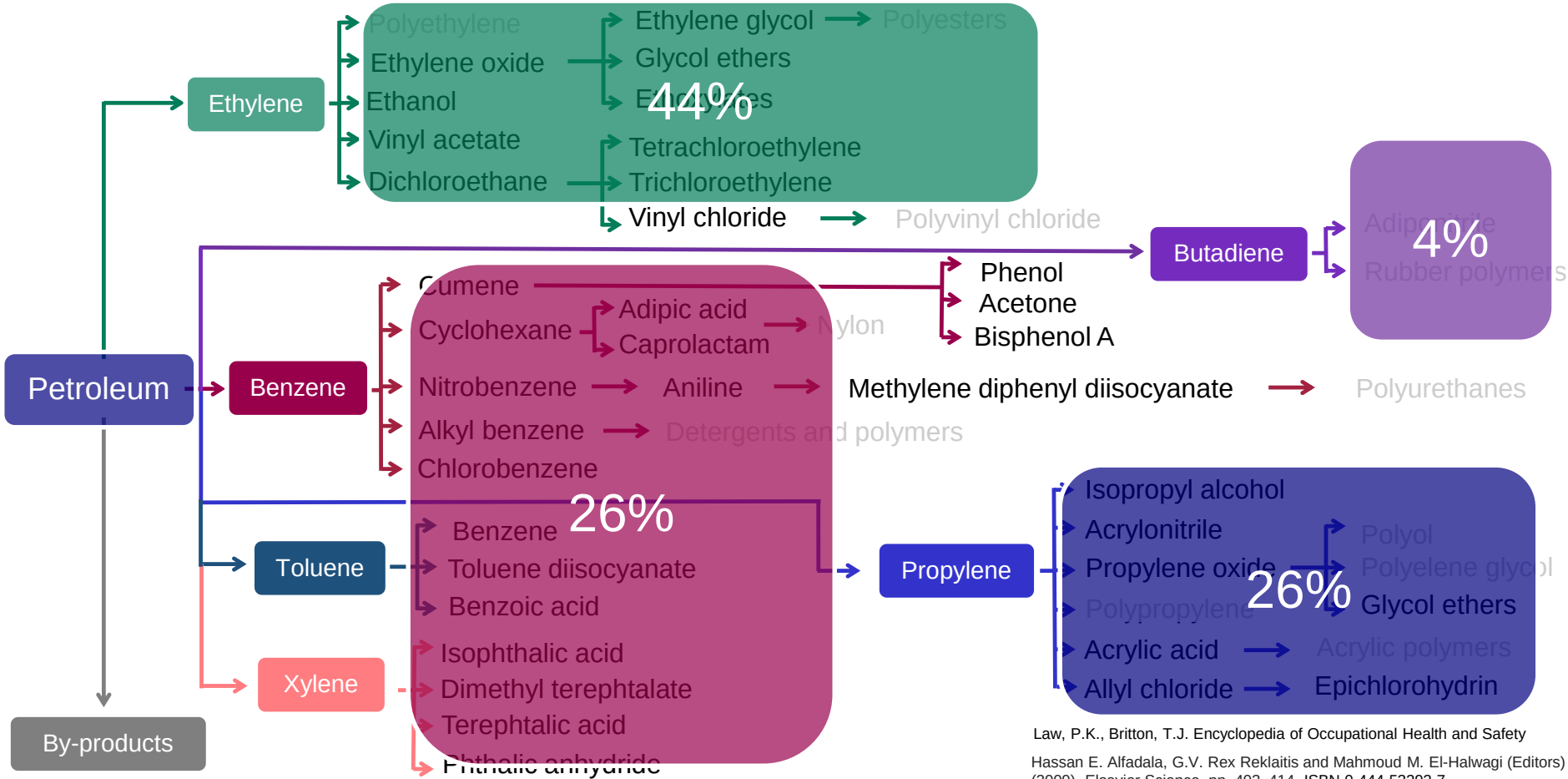

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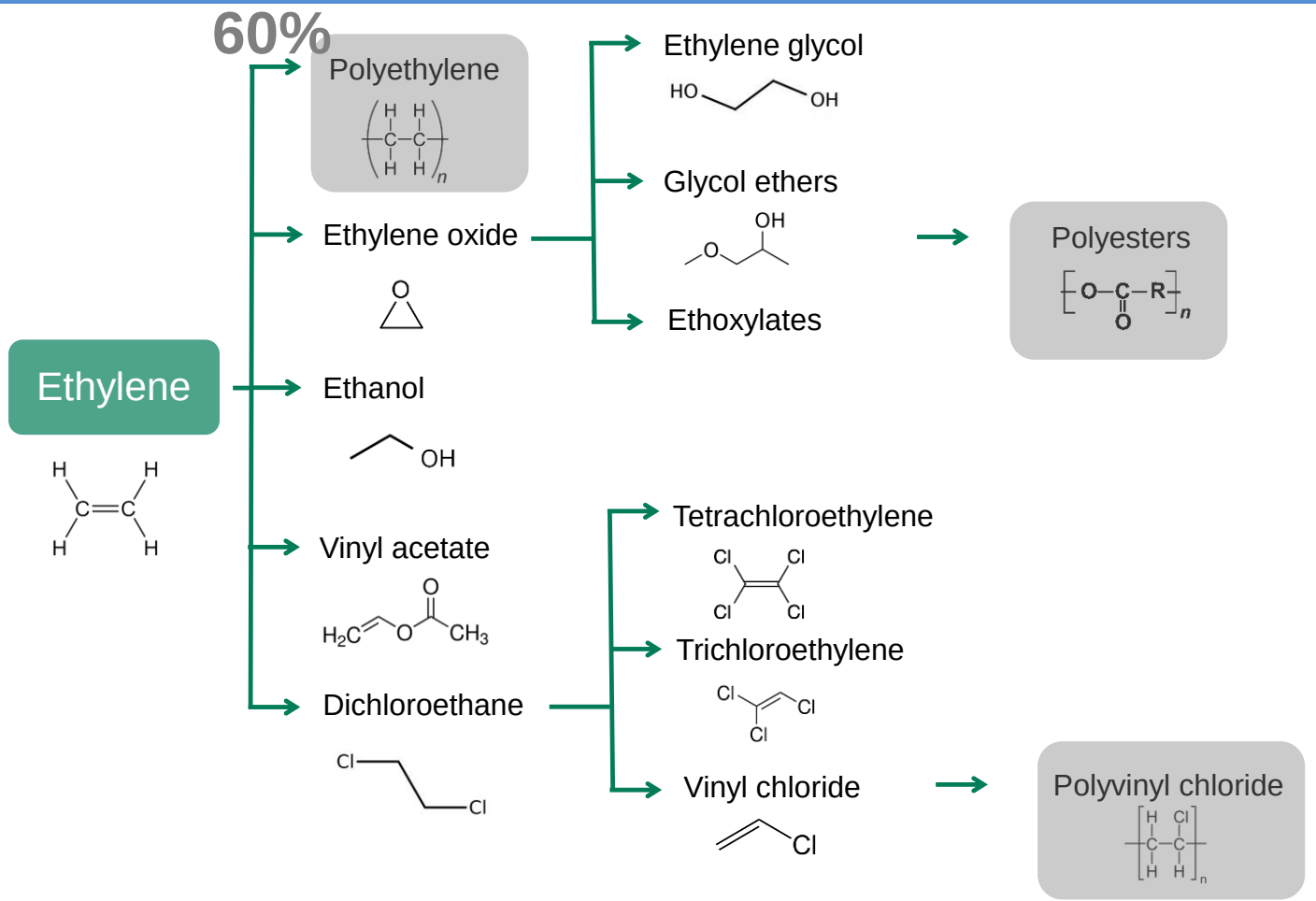
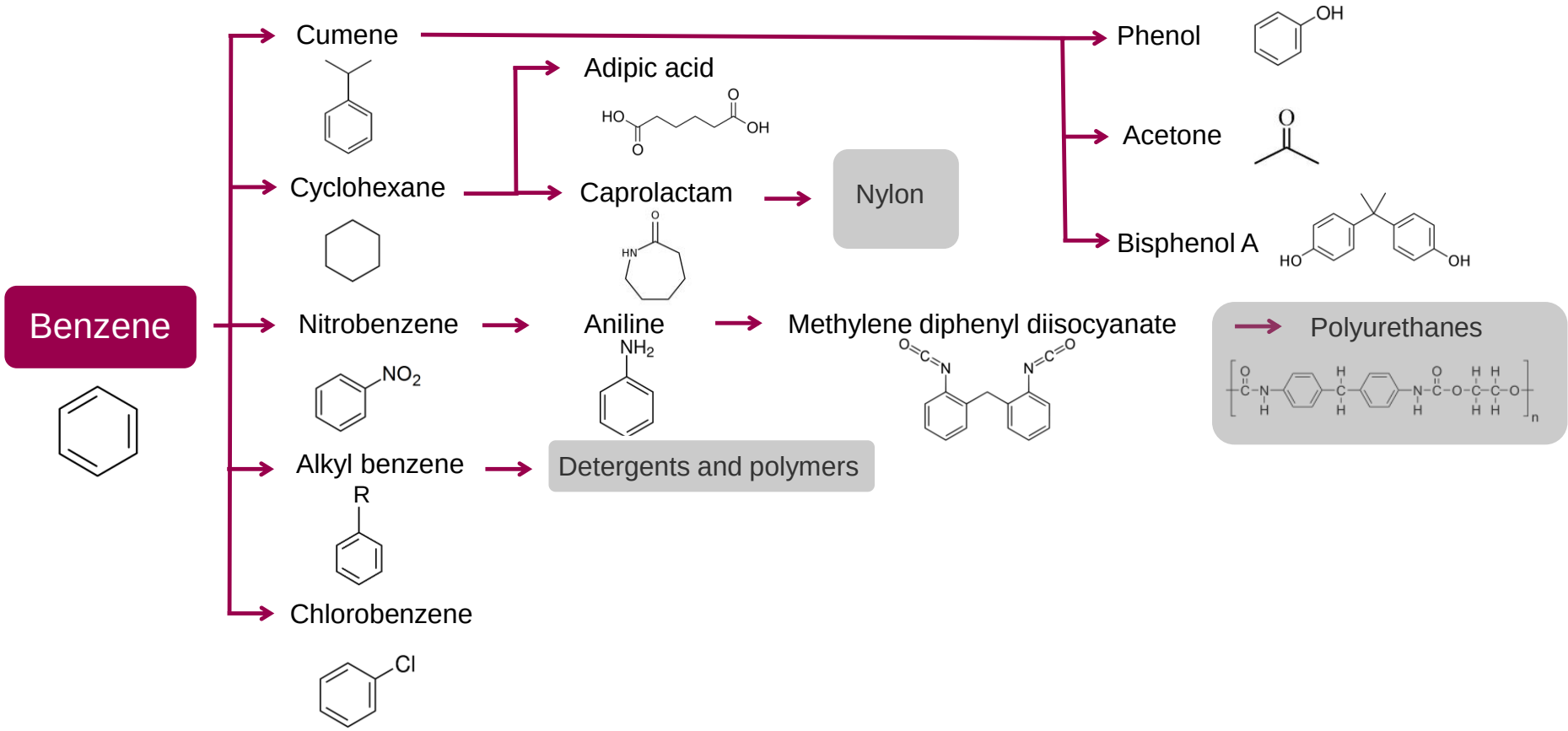
Ethylene Derivatives

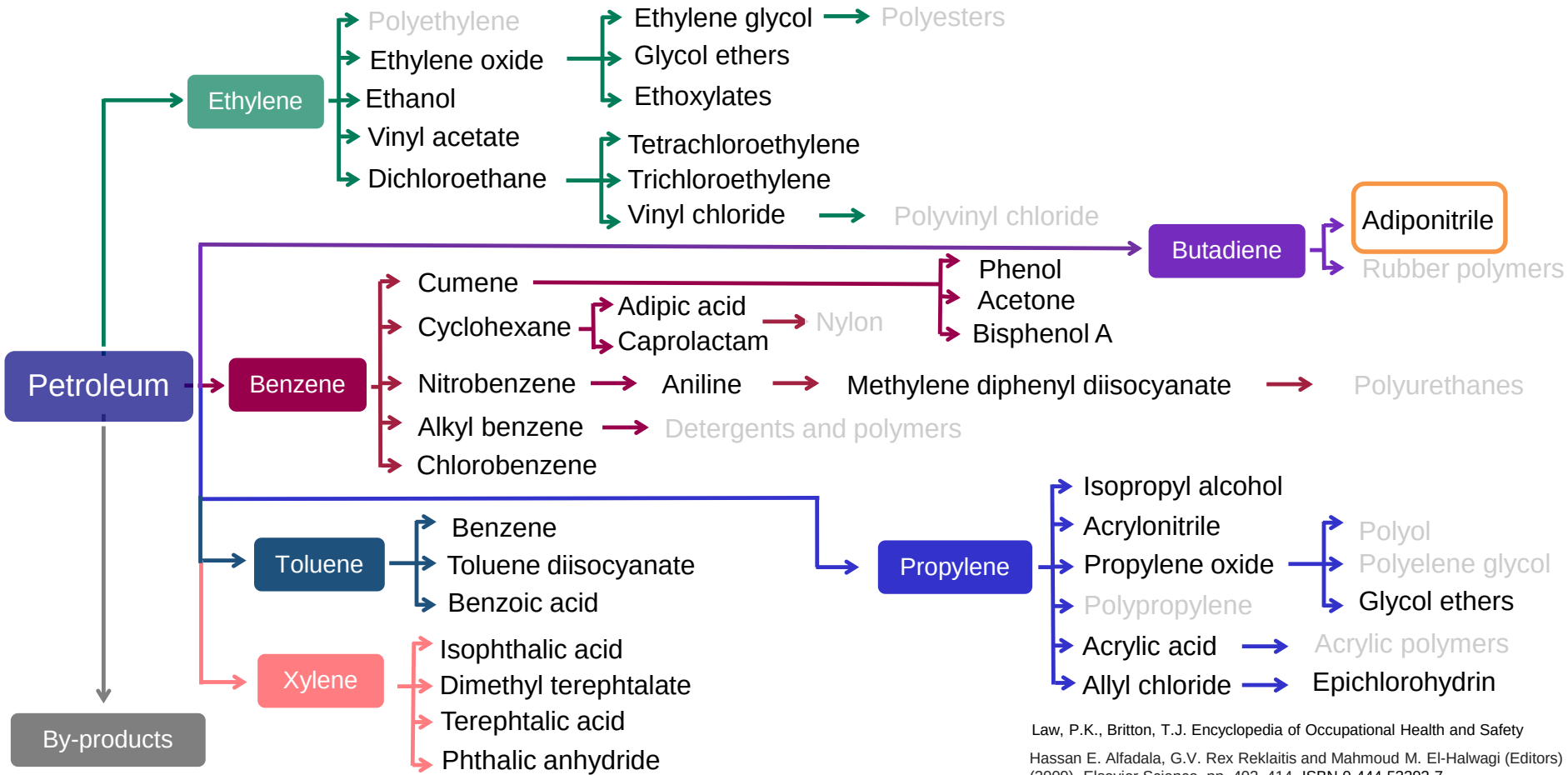


Approximately **44%** of petrochemical feedstock

Benzene Derivatives



Industrial Petrochemical Processes



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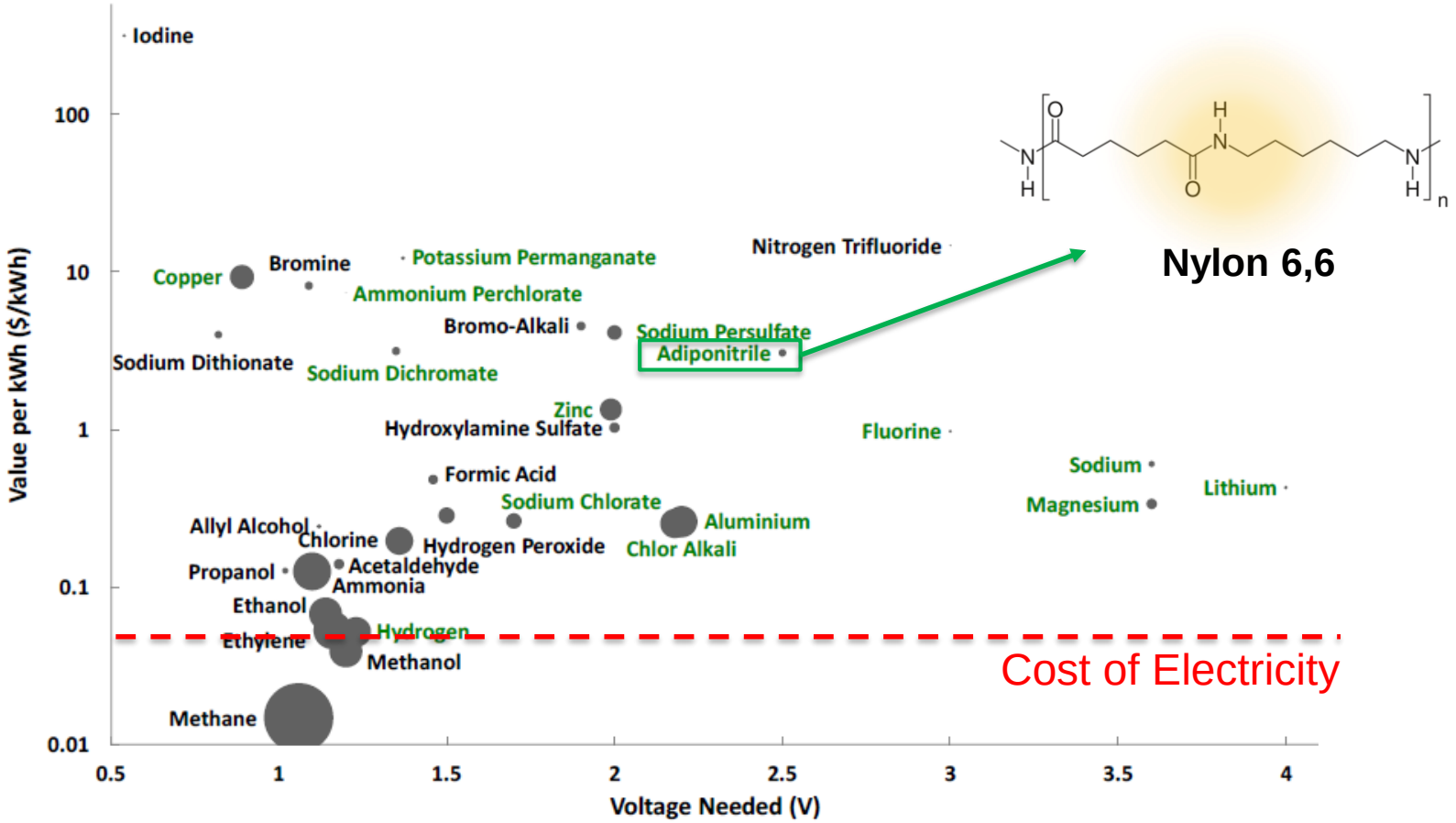
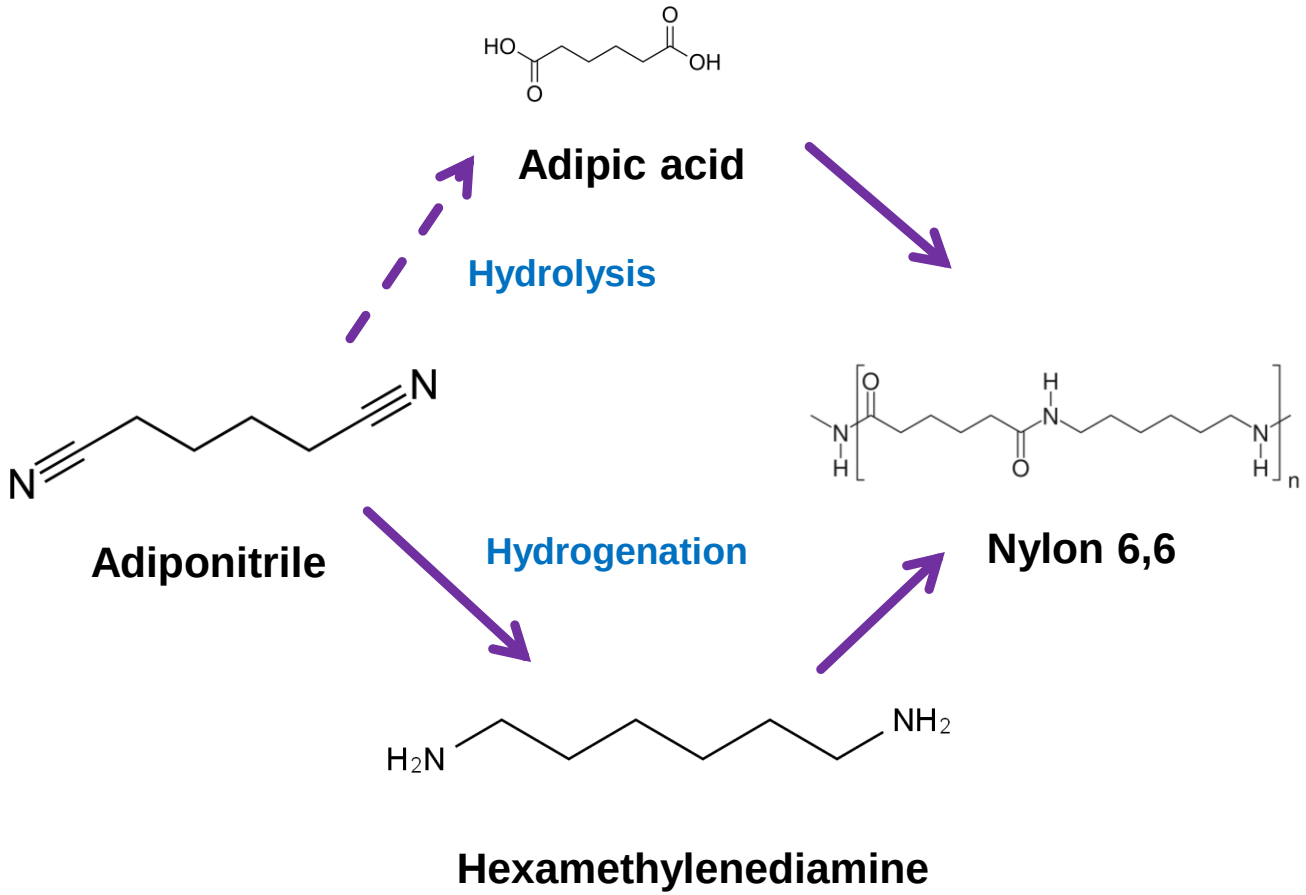
Targeting high potential processes



Palmer, Saadi, McFarland, ACS Sustainable Chem. Eng., **2018**, *6* (5), pp 7003–7009

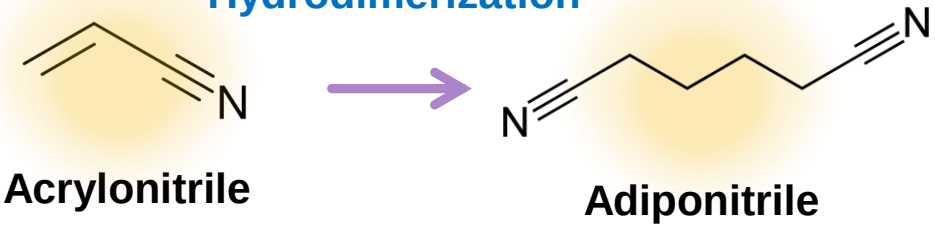
Adiponitrile: Nylon 6,6's key precursor



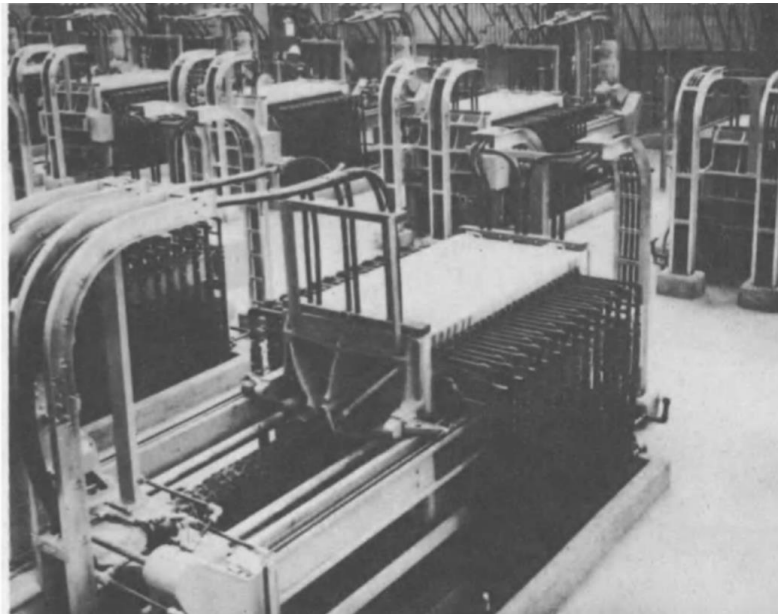
Importance of the electrochemical route

>500K tons/year

Electro Hydrodimerization



Acrylonitrile → **Adiponitrile**

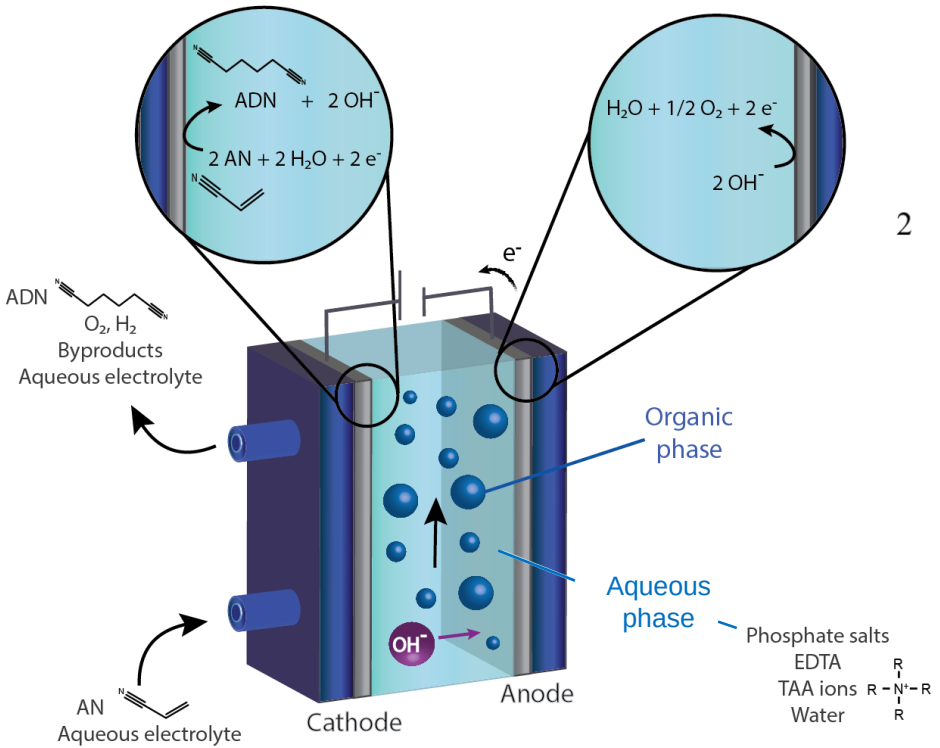


Manuel M. Baizer

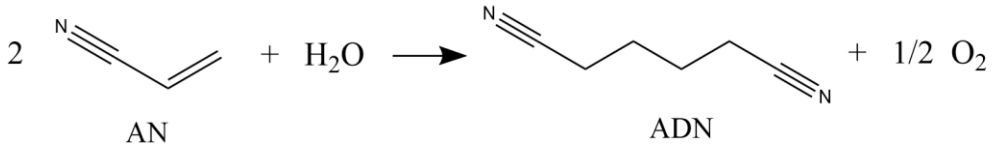
Monsanto, 1963

[1]G. Botte, *Electrochem. Soc. Interface*, 2014, **23**, 49-55.

Electrohydrodimerization of AN to ADN



Overall reaction



Goal

High selectivity

High throughput

High energy conversion efficiency

Big Challenges in Organic Electrosynthesis at Scale

Box 1. Key Challenges of Organic Electrosynthesis

Limited Stability of Electrolytes

Scalable electrochemical processes rely on inexpensive aqueous electrolytes. These electrolytes have a limited electrochemical stability window dictated by the onset potential of the water oxidation or reduction reaction: the hydrogen evolution reaction (HER) in the cathode and the oxygen evolution reaction (OER) in the anode. If the desired transformation requires reductive potentials below or oxidative potentials above those of water, the organic reaction will face competition from the HER and the OER, respectively, lowering the energy conversion efficiency.

Low Reactant Solubility

Most organic species suffer from low solubility in aqueous electrolytes. Under steady-state operation, the diffusion rate of reactants from the bulk electrolyte to the electrode needs to match their consumption rate at reactive sites. Low concentrations of organic reactants in the bulk electrolyte lead to slow diffusion rates, resulting in limitations on the maximum attainable production rate. Furthermore, high electrochemical reaction rates lower the local concentration of organic species in the near-electrode region. This change in reactant local concentration affects reaction selectivity and the distribution of various electrosynthetic products.

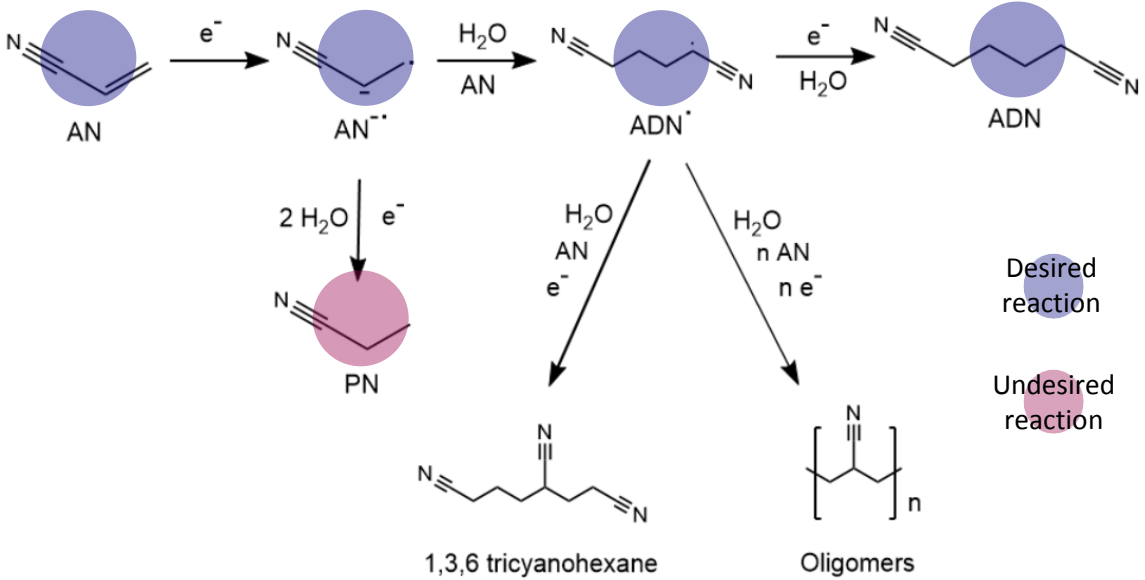
Selectivity Over Reaction Pathways

Organic electrosynthesis is often characterized by the presence of several reaction pathways, leading to desired products or undesired by-products. The operation of electrosynthetic reactors with fluctuating renewable sources can impose varying reaction potentials, which trigger strong variations in reaction pathways, affecting selectivity and production rates.

"Conquering the challenges currently hindering large-scale organic electrosynthetic processes would greatly benefit many sectors of chemical manufacturing"

Blanco, Modestino. **Trends in Chemistry**, Vol 1, No. 1

Desired and undesired reactions

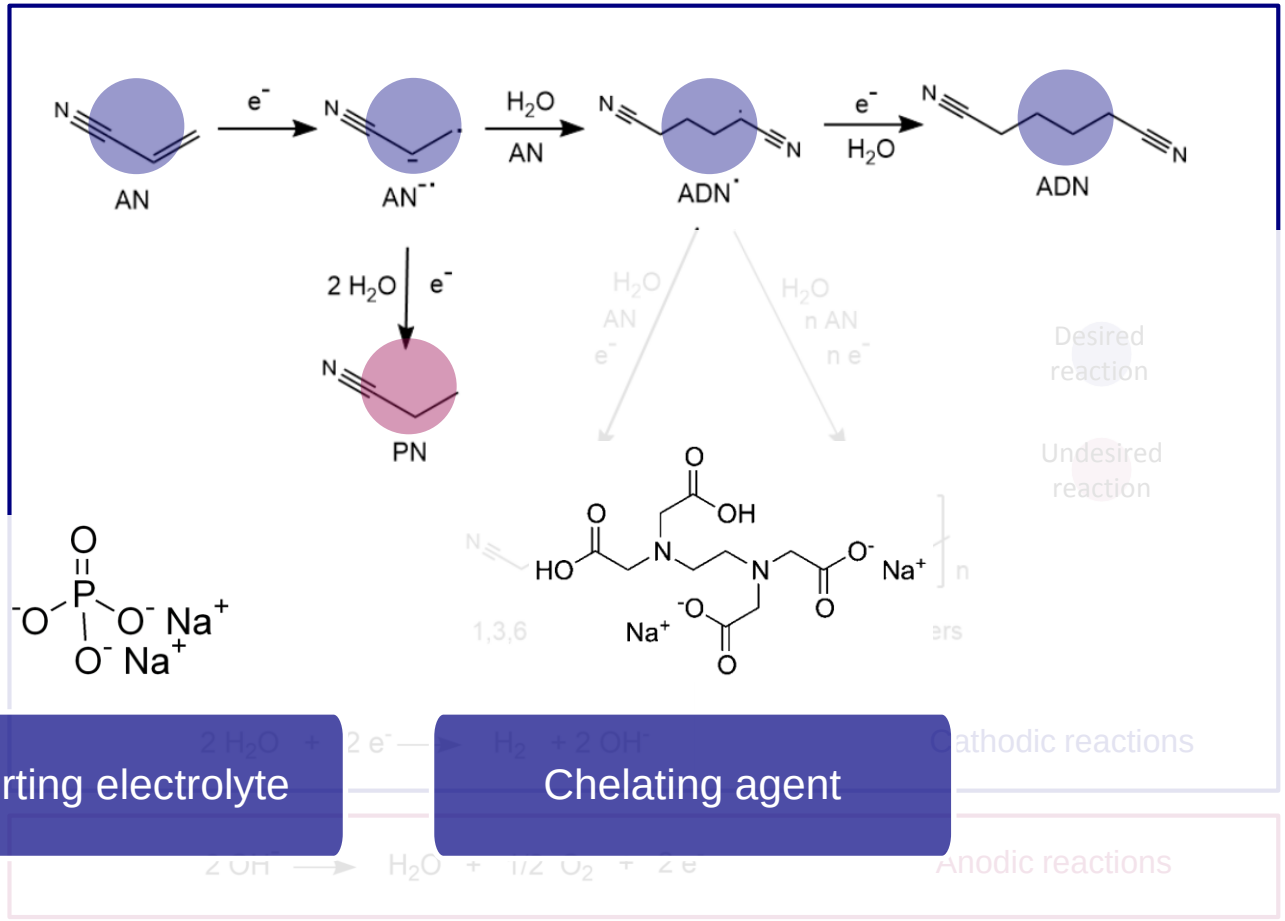


$2\ H_2O + 2\ e^- \longrightarrow H_2 + 2\ OH^-$ Cathodic reactions

$2\ OH^- \longrightarrow H_2O + 1/2\ O_2 + 2\ e^-$ Anodic reactions

Daniela Blanco

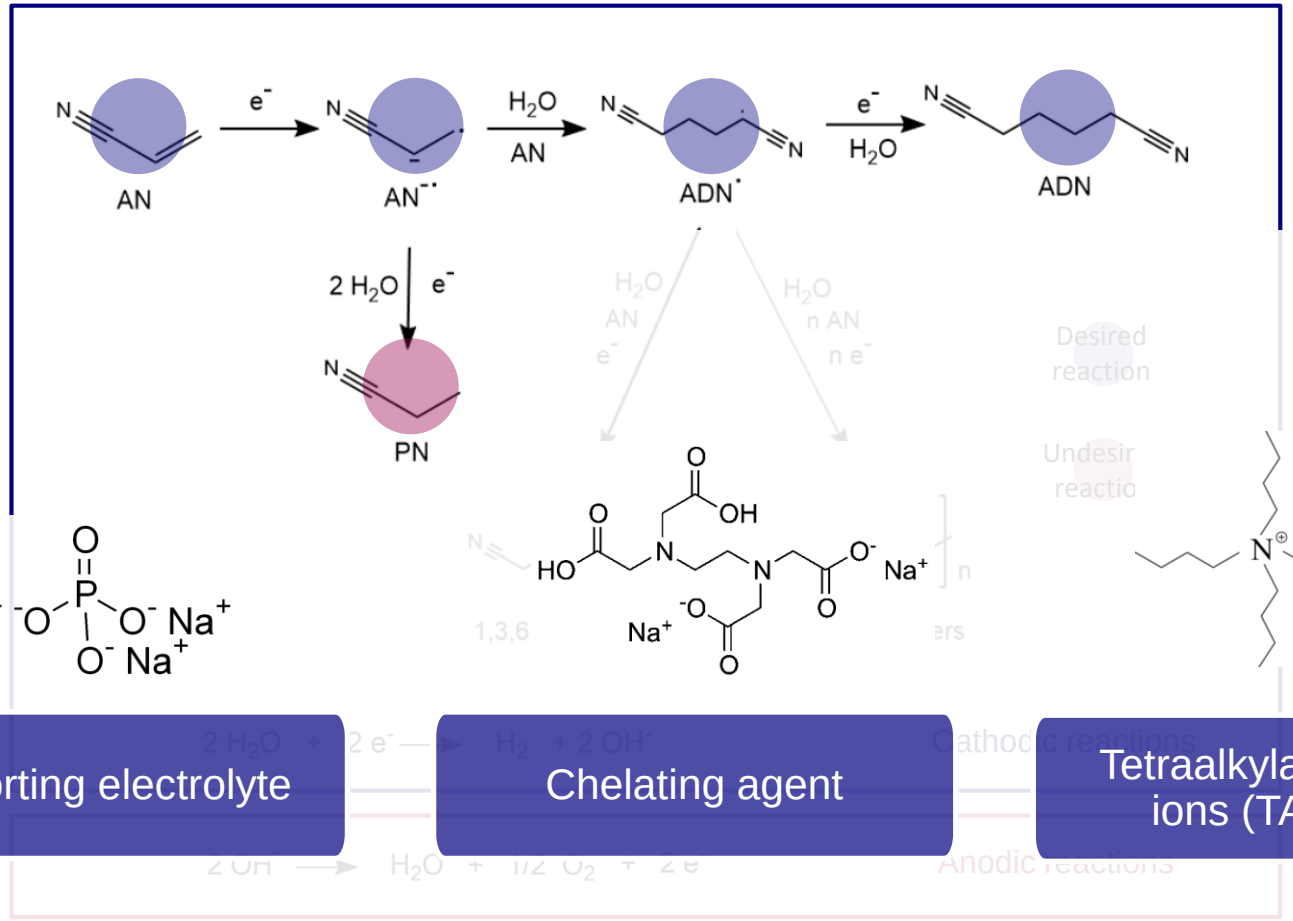
Desired and undesired reactions

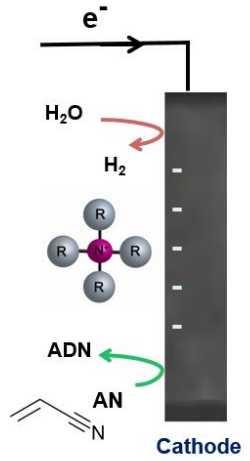


Supporting electrolyte

Chelating agent

Desired and undesired reactions



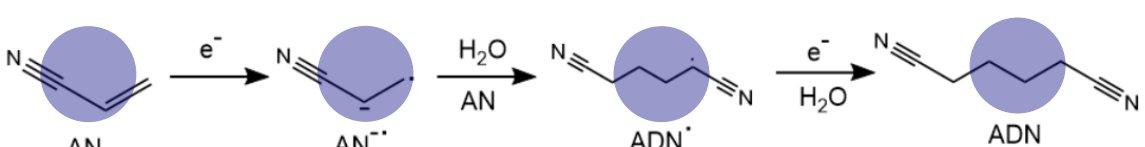


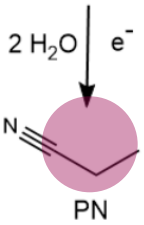
Supporting electrolyte

Chelating agent

Tetraalkylammonium ions (TAA ions)

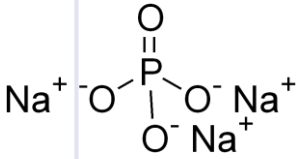
Desired and undesired reactions

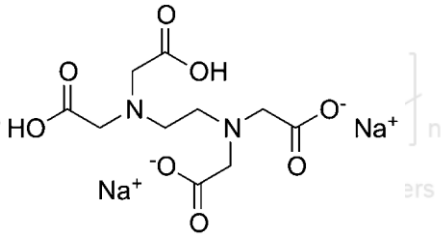


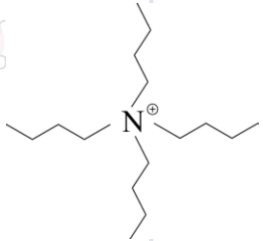


pH 7-11

Intermediate – basic pH





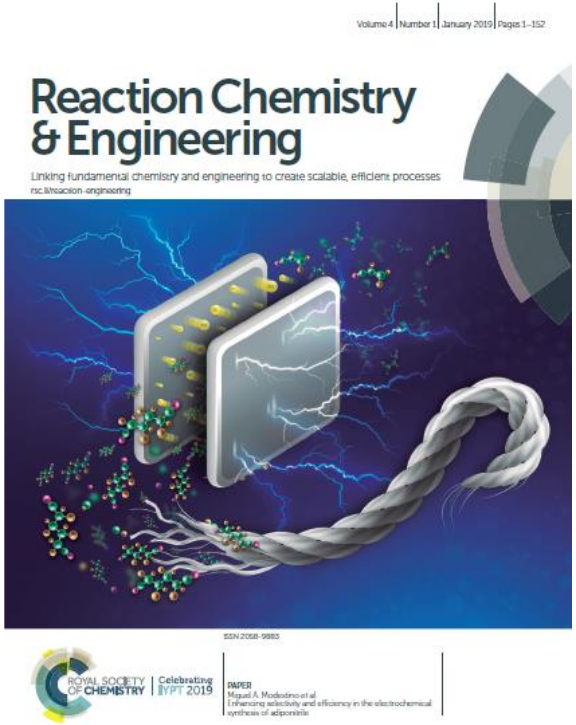


Supporting electrolyte

Chelating agent

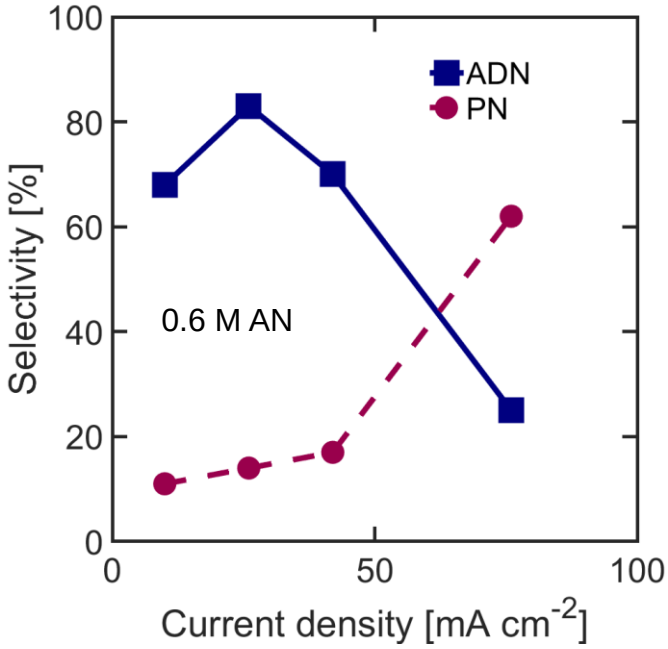
Tetraalkylammonium ions (TAA ions)

State-of-the-art ADN electrosynthesis



83%
selectivity
towards ADN
at **-26 mA cm^{-2}**

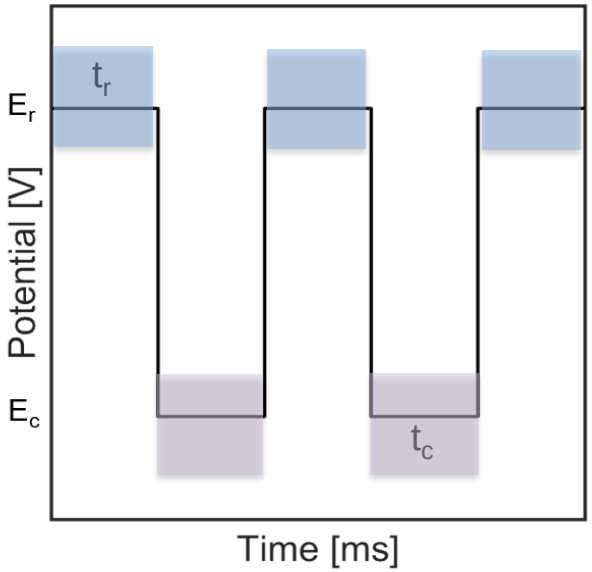
0.6 M AN
0.5 M Na_3PO_4
0.02 M TBA OH
0.03 M EDTA

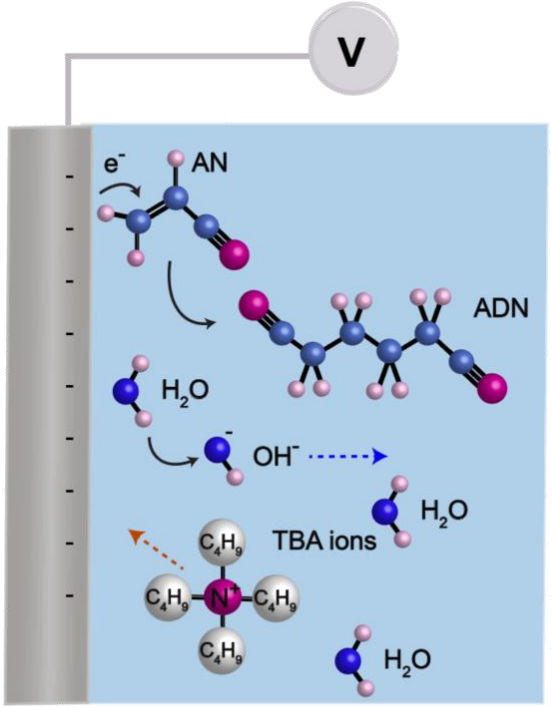


Blanco et. al, React. Chem. Eng., 2019, 4, 8–16

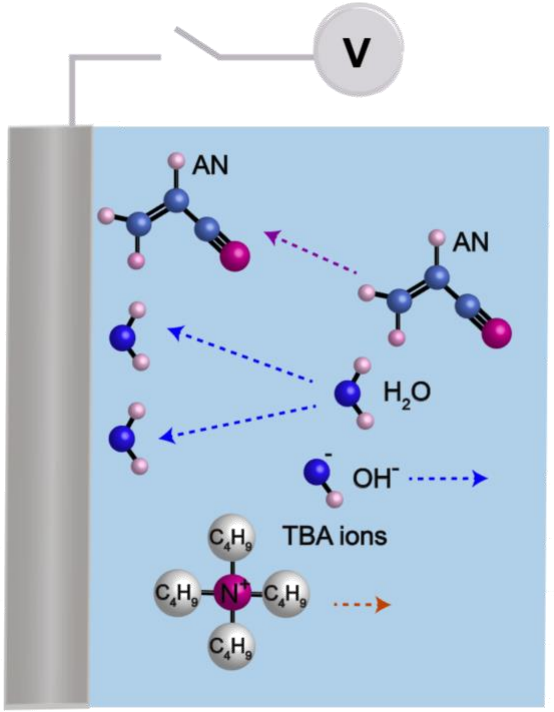
How can we improve transport control?

Controlling dynamics through pulsed electrosynthesis





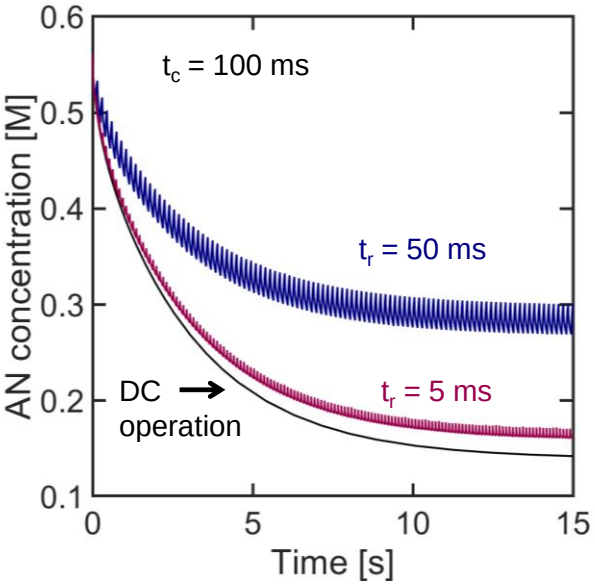
Cathodic time

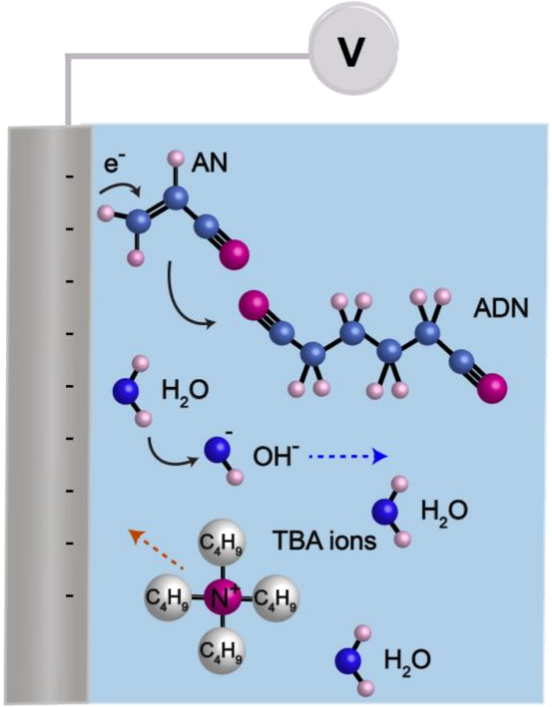


Resting time

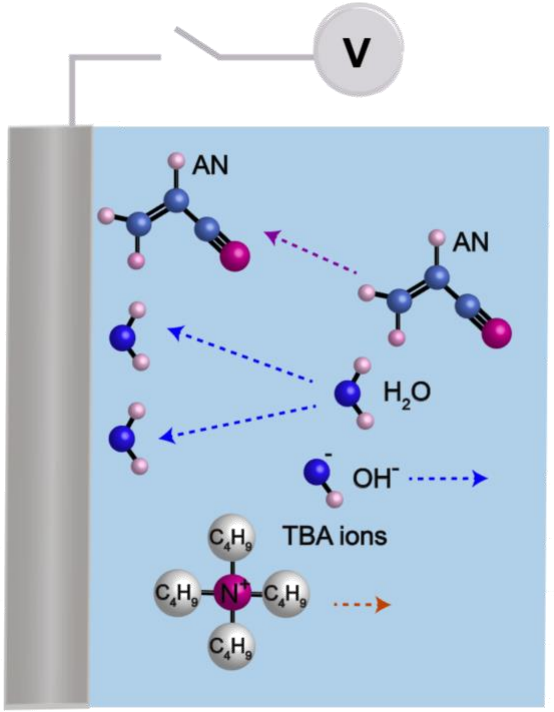
Controlling dynamics through pulsed electrosynthesis

Transient mass transport model



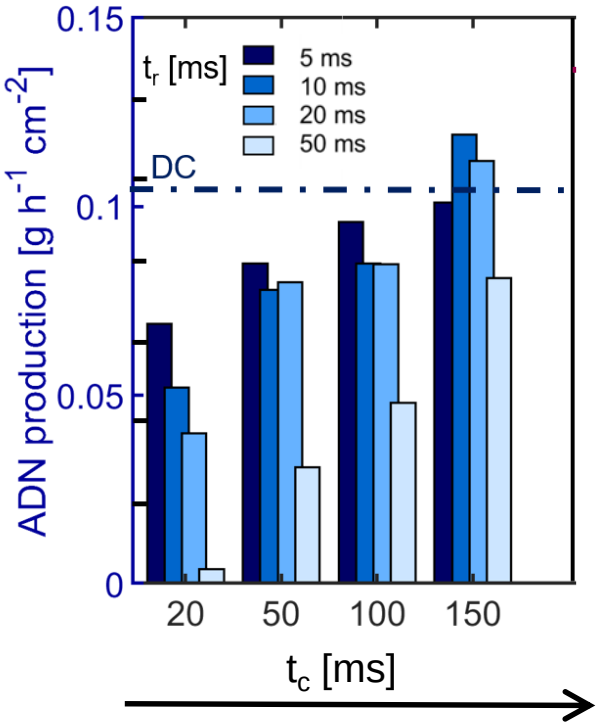


Cathodic time



Resting time

Effect of cathodic (t_c) and resting (t_r) times



E_c: -3.5 V vs Ag/AgCl (-60 mA cm^{-2})
E_r: 0V vs Ag/AgCl

↑ t_c → ↑ ADN production

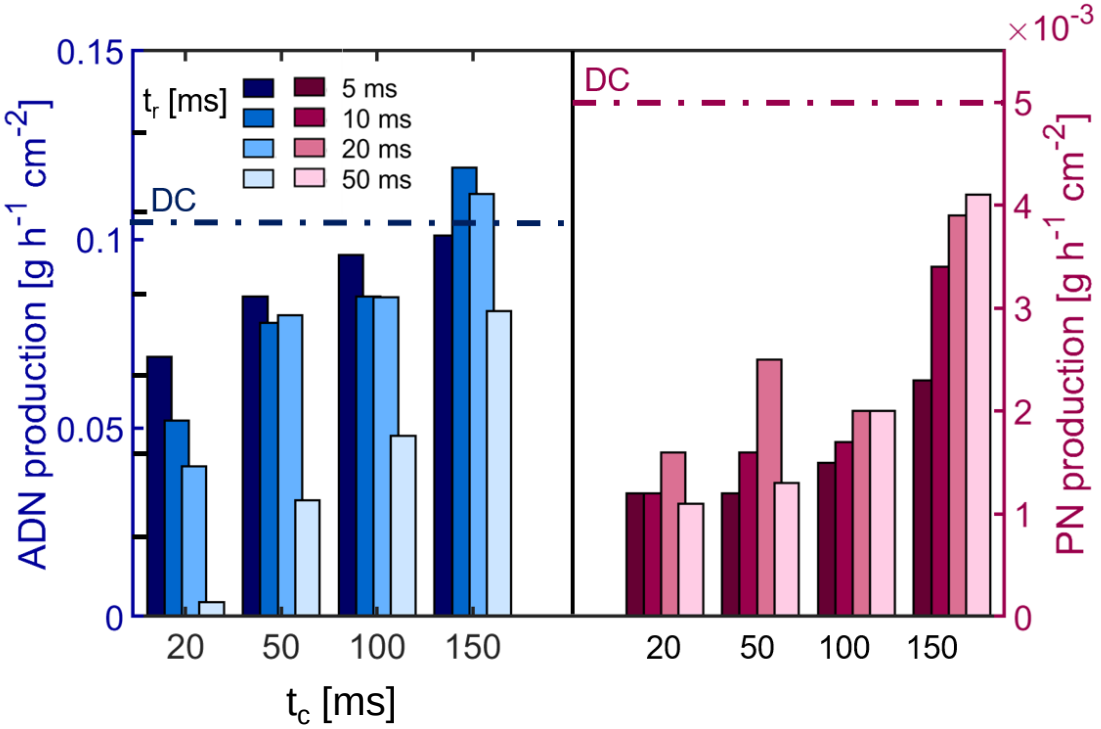
↑ t_r → ↓ ADN production

Longer reaction times increase AN conversion and ADN production

20% net increase in ADN production

Blanco et al. , ***PNAS***, 2019, **116**, 17683-17689.

Effect of cathodic (t_c) and resting (t_r) times



80% decrease in PN production

Mitigation of mass transport limitations

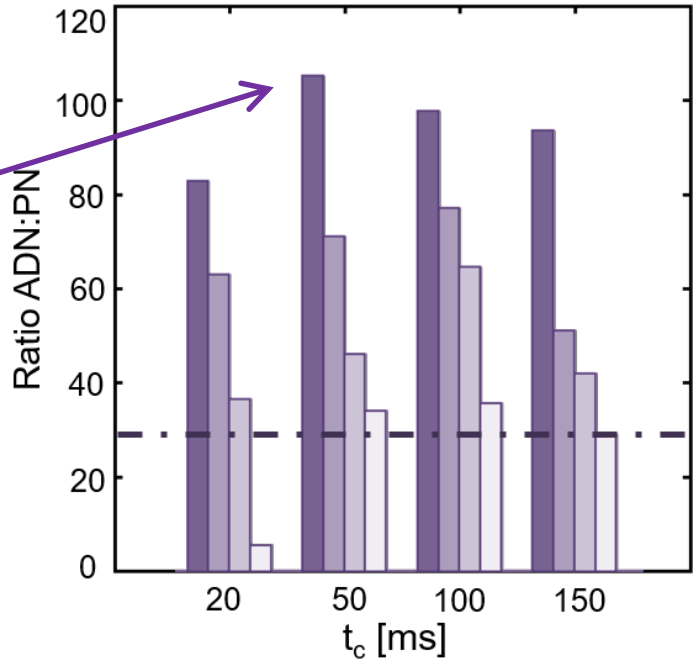
E_c: -3.5 V vs Ag/AgCl (-60 mA cm^{-2})
E_r: 0V vs Ag/AgCl

Blanco et al. , ***PNAS***, 2019, **116**, 17683-17689.

Effect of cathodic and resting times

250%

improvement in ADN:PN ratio



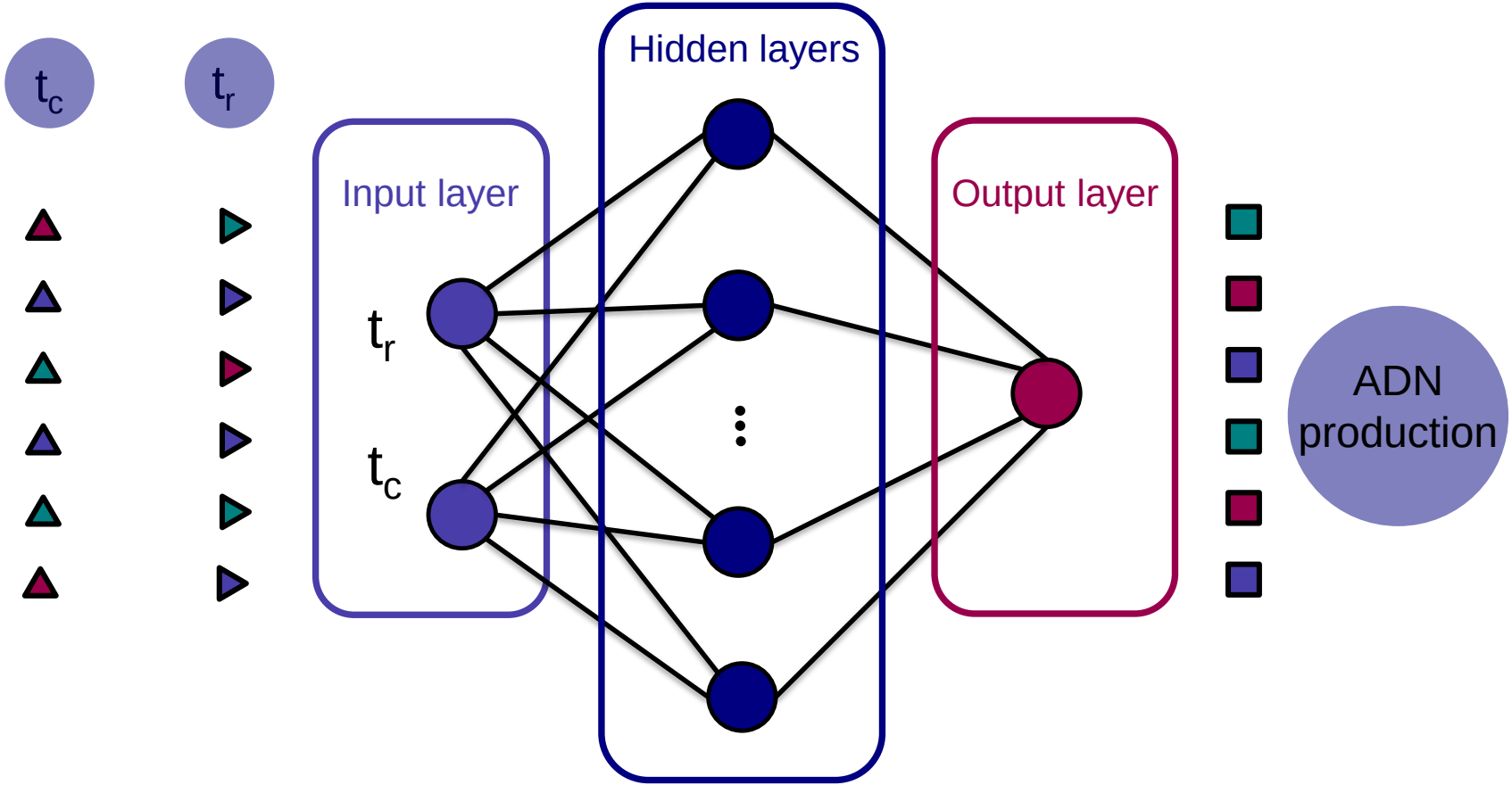
E_c: -3.5 V vs Ag/AgCl (-60 mA cm^{-2})

E_r: 0V vs Ag/AgCl

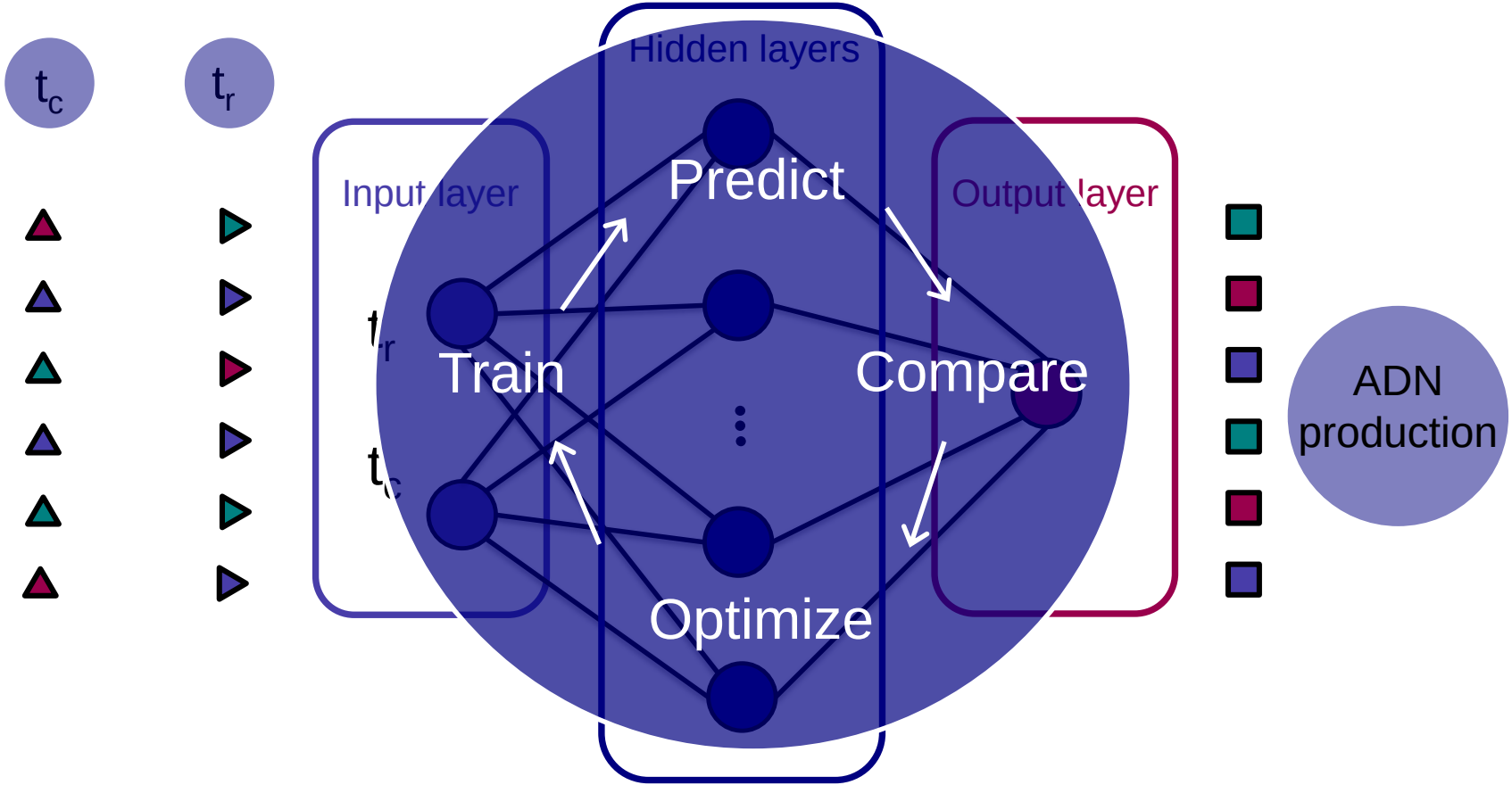
Blanco et al. , ***PNAS***, 2019, **116**, 17683-17689.

Data-driven Optimization

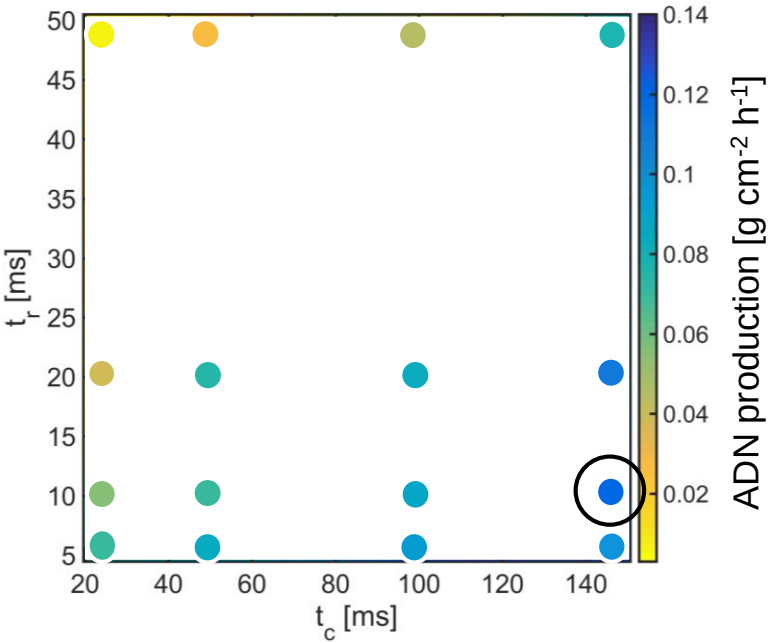
Functioning of Artificial Neural Networks



Functioning of Artificial Neural Networks



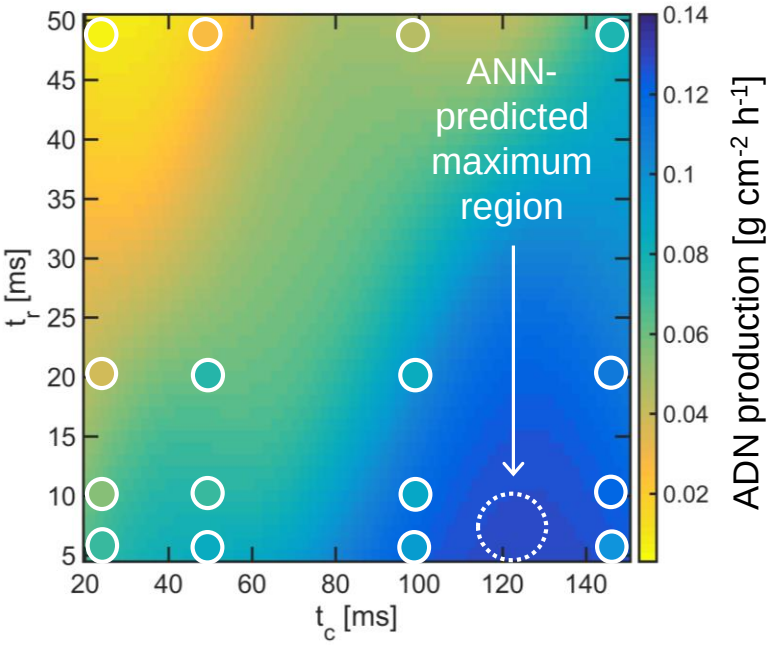
ANN-predicted ADN production

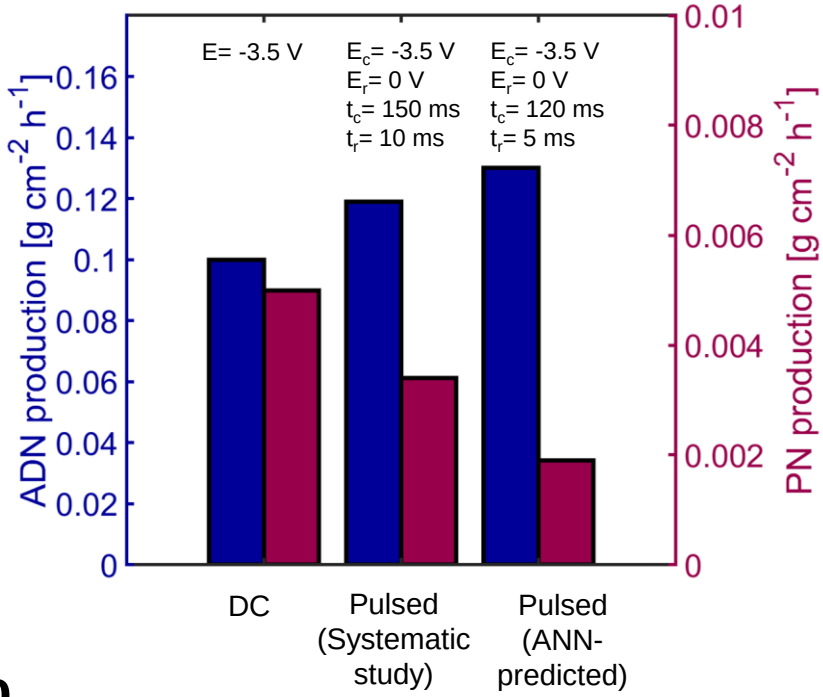


20%
increase

Blanco et al. , ***PNAS*,** 2019, **116**, 17683-17689.

ANN-predicted ADN production





20% → **30%** increase

Blanco et al. , ***PNAS***, 2019, **116**, 17683-17689.

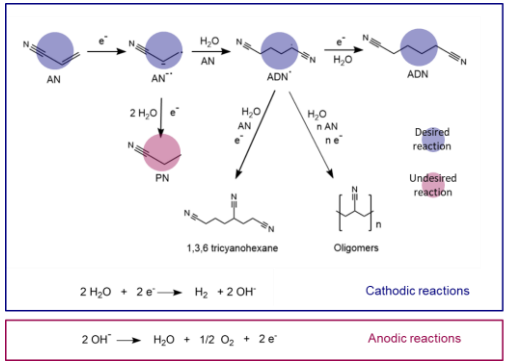
Engineering Electrochemical Manufacturing

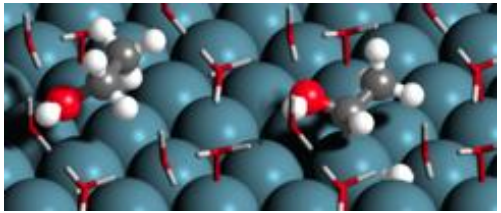
Reaction Development

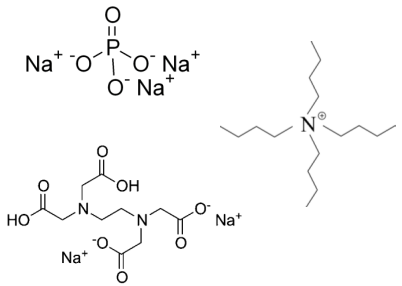
Electrolyte Engineering

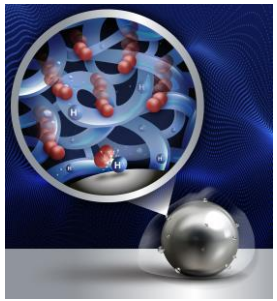
Operational Control

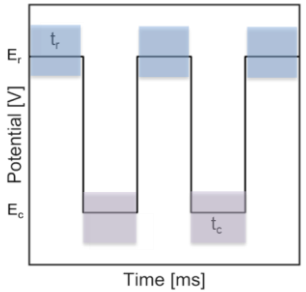
Data Analytics

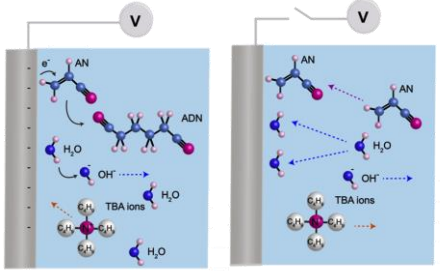


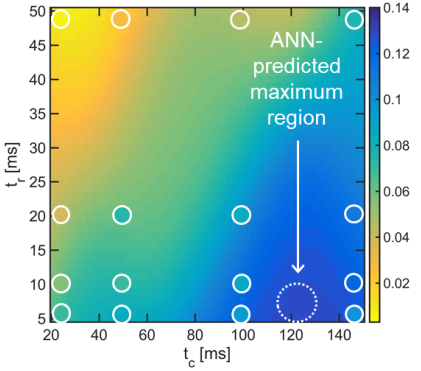










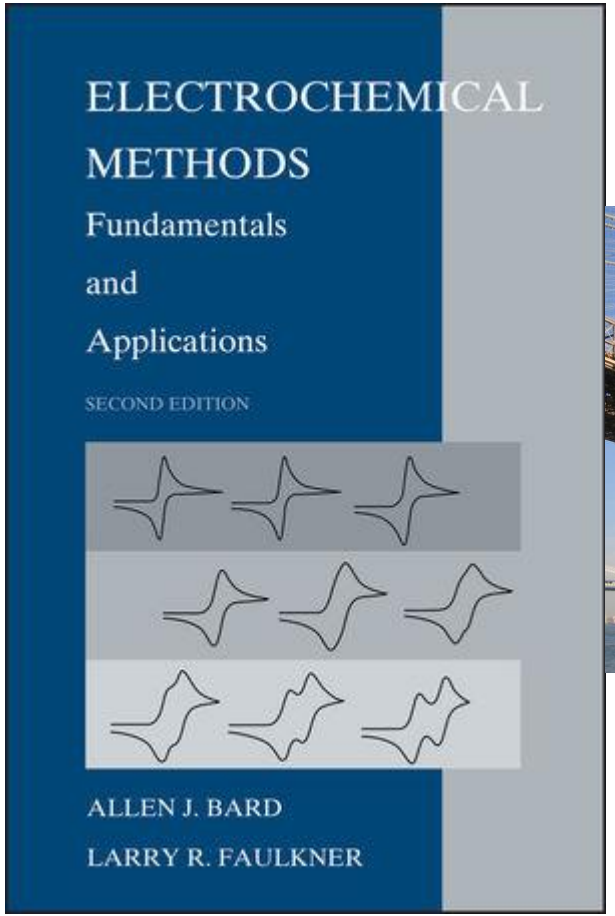


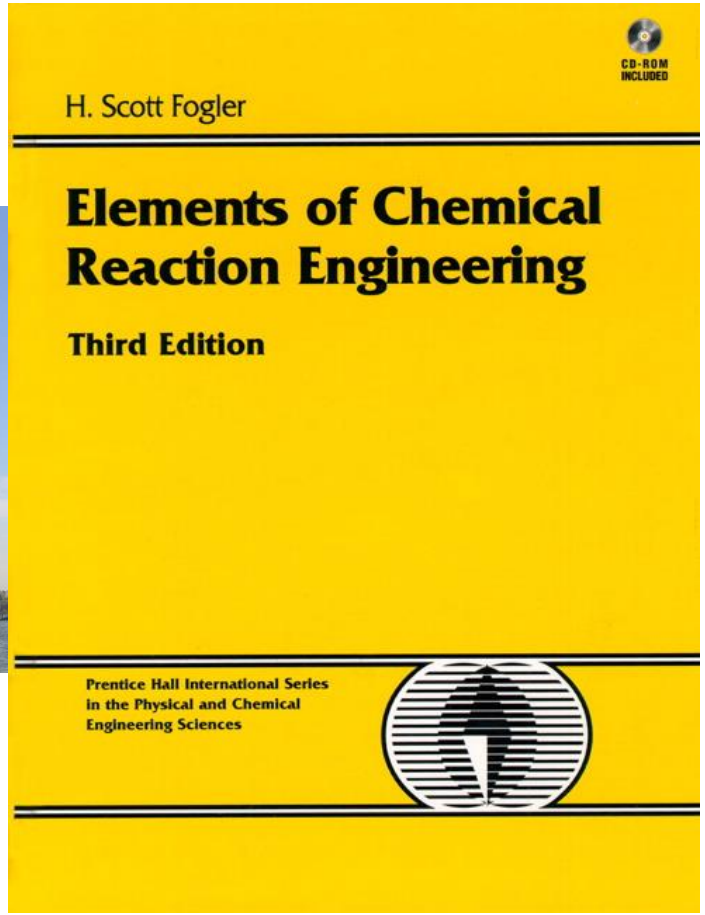
Engineering Electrochemical Manufacturing

Reaction Development	Electrolyte Engineering	Operational Control	Data Analytics
Electrosynthesis Discovery	Electrolyte Formulation	Transport Phenomena and Kinetics	Machine Learning (aka statistics)
Mechanistic Understanding	Ionomer Design	Reaction Engineering & Reactor Design	Automation & Control
Electrocatalyst Development	In-operando EDL		Mixed Data/Modeling

Multiscale Theory and Simulations / Characterization

Electrochemical Reaction Engineering Toolkit





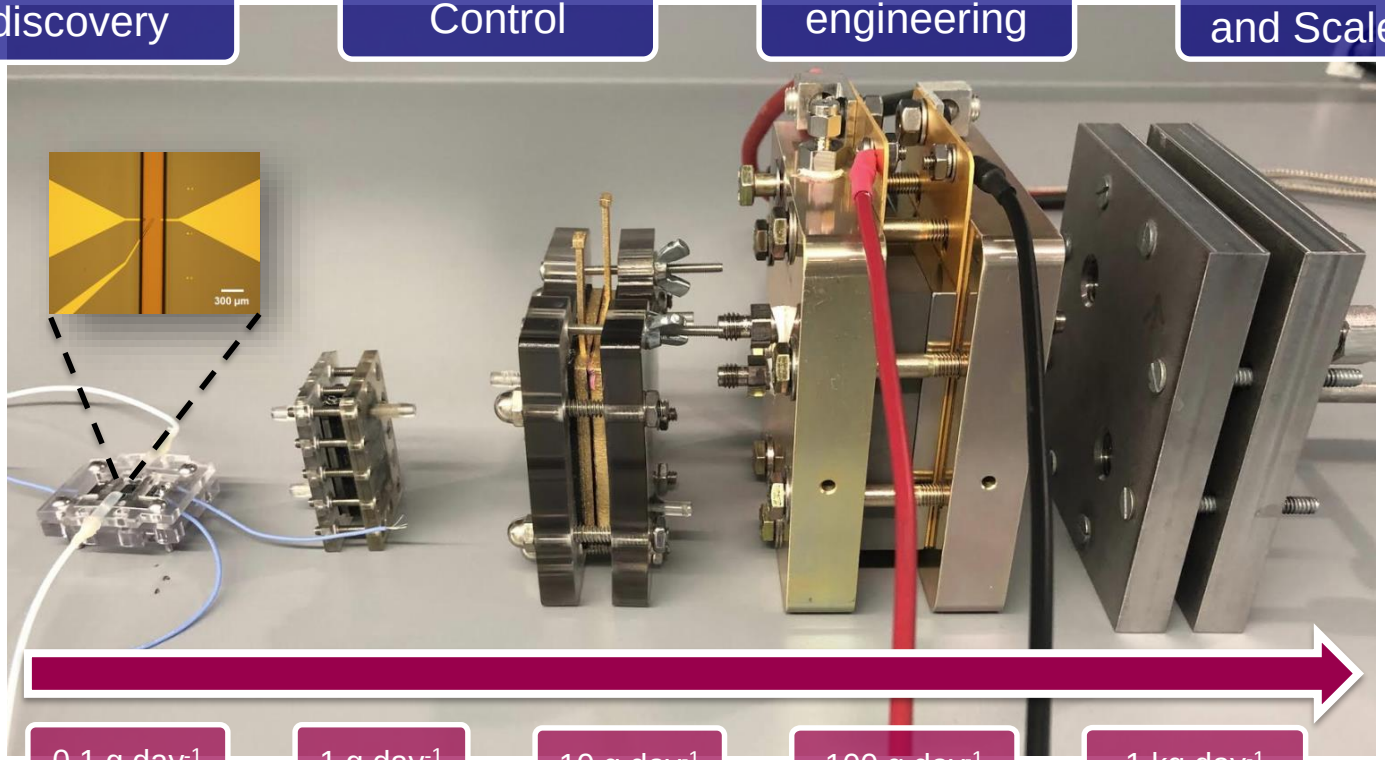
Electrochemical Reaction Engineering Toolkit

Reaction discovery

Environment Control

Reactor engineering

Prototyping and Scale-up



Microfluidics

Electrochemical Stacks

0.1 g day^{-1}

1 g day^{-1}

10 g day^{-1}

100 g day^{-1}

1 kg day^{-1}

Taking Electrosynthesis to Scale

sunthetics

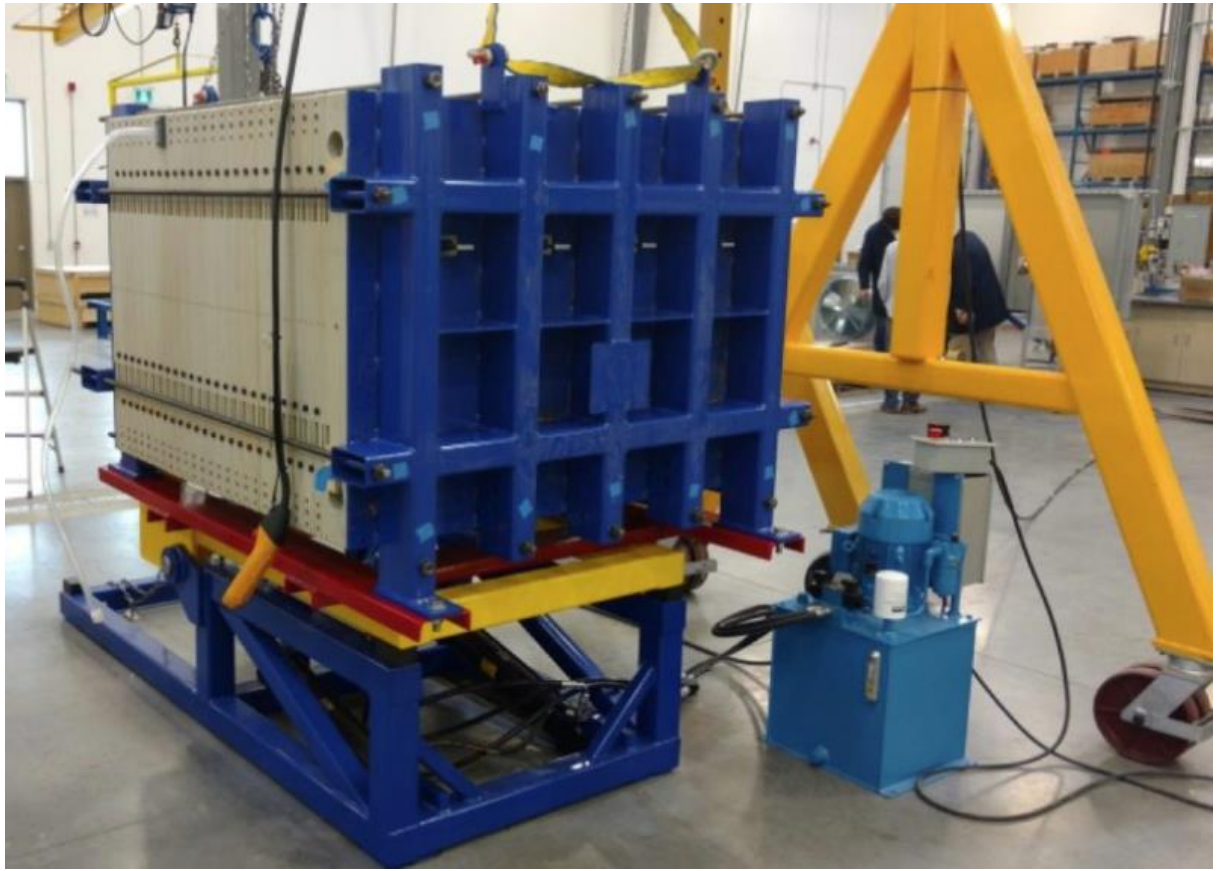
opus 12

Electrosynthesis

NORAM

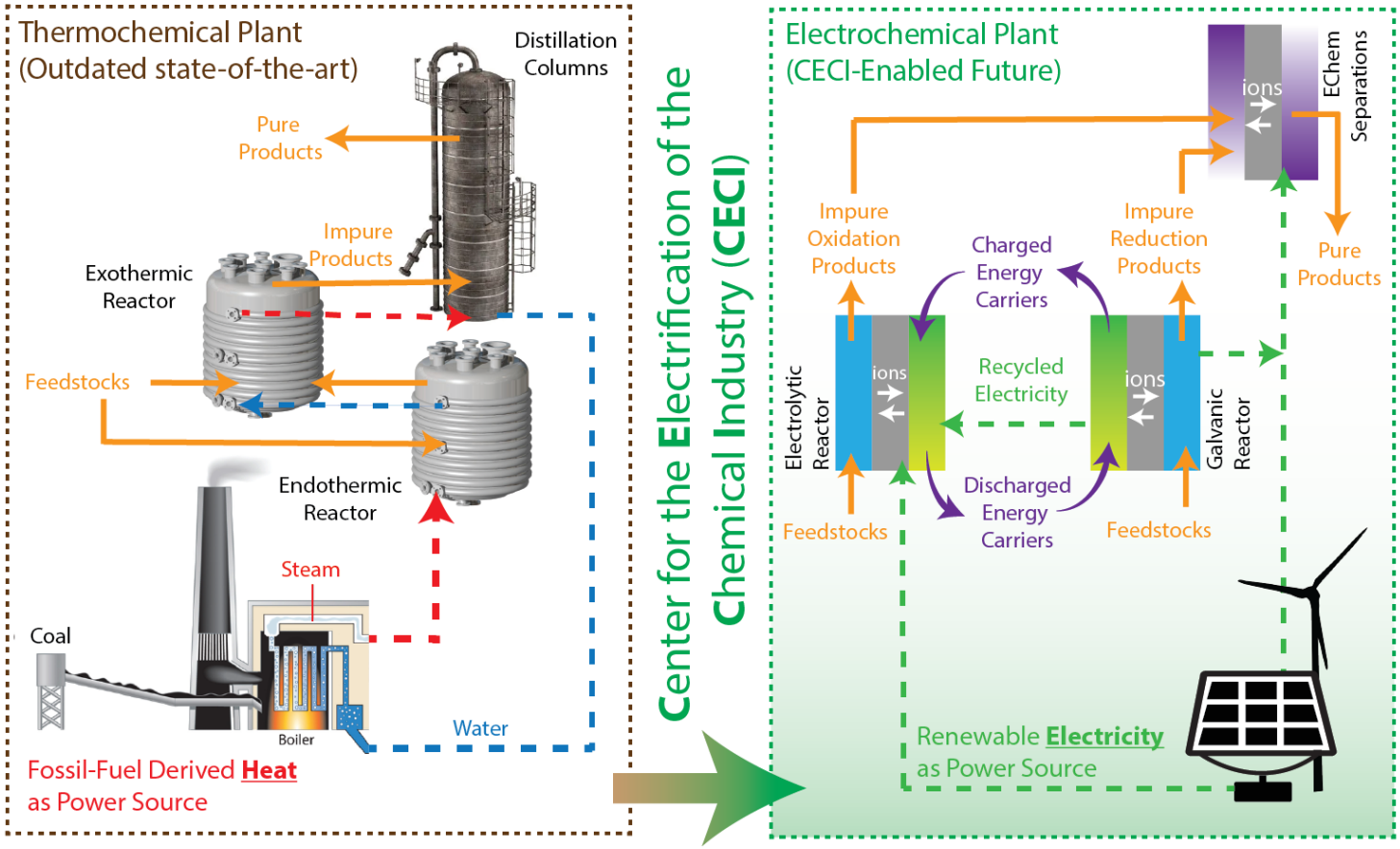
Dioxide Materials™
The CO_2 Recycling Company™

AIR C·O



http://dev.noram-eng.com/electrochemical/

Planning an Electrifying Engineering Research Center

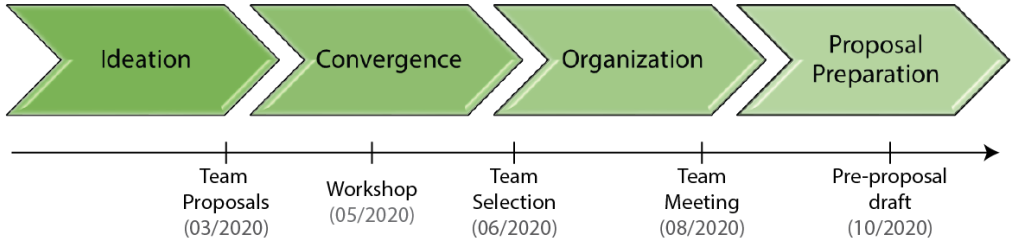


Building an ERC from the ground up: **Participate!**

Calling Teams in the Following Areas:

Components	Unit Operations
Membranes Electrocatalysts and Catalysts Redox Energy Carriers and Absorbers	Reactors Separation Units
System Integration	**Societal Impact**
Plant Level Integration Grid Level Integration	Technoeconomic and Lifecycle Analysis Workforce Development Entrepreneurship and Knowledge Transfer

Timeline



wp.nyu.edu/ceci

Eray Aydil

Yury Dvorkin

Sanat Kumar

Miguel Modestino

COLUMBIA UNIVERSITY

NYU

Thank you

Ph.D. Students:

Toshihiro Akashagi

Andrea Angulo

Daniela Blanco

Adlai Katzenberg

Daniel Frey

Postdocs:

Yasmine Hajar

Debdyuti Mukherjee

B.S./M.S. Students:

Azan Brar

Brian Chen

Aaliyah Dookith

Andrea Quispe

Xinshu Shang

Kaylee Dunnigan

Research Staff:

Bryan Lee

www.modestinogroup.com