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
A short story about myself

Venezuela

1985 - 2003

The death of Venezuela’s Humboldt glacier
Solar in sectors that SUFFER from INTERMITTENCY

- Residential: 21%
- Commercial: 19%
- Industrial: 31%
- Transportation: 29%
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

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.

Terry et al. (1997). J. AIChE, 7, 43, 1709

Electrochemical Approach Impact Other Separations

**Olefins**


Terry et al. (1997). J. AIChE, 7, 43, 1709

**CO₂ capture**


**Water Purification**

How about Reaction Processes?
Industrial Petrochemical Processes

Petroleum

- Ethylene
  - Ethylene oxide
  - Ethanol
  - Vinyl acetate
  - Dichloroethane

- Benzene
  - Cumene
  - Cyclohexane
  - Nitrobenzene
  - Alkyl benzene
  - Chlorobenzene

- Toluene
  - Benzene
  - Toluene diisocyanate
  - Benzoic acid

- Xylene
  - Isophthalic acid
  - Dimethyl terephthalate
  - Terephthalic acid
  - Phththalic anhydride

- Propylene
  - Benzene
  - Toluene diisocyanate
  - Benzoic acid

- By-products

- Ethylene glycol
- Glycol ethers
- Ethoxylates
- Tetrachloroethylene
- Trichloroethylene
- Vinyl chloride
- Polyethylene
- Polyesters
- Polyvinyl chloride
- Adiponitrile
- Rubber polymers
- Polyurethanes
- Polyol
- Polyethylene glycol
- Glycol ethers
- Acrylic polymers
- Epichlorohydrin

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

- Ethylene
  - Polyethylene
  - Ethylene oxide
  - Ethanol
  - Vinyl acetate
  - Dichloroethane
  - Ethylene glycol
  - Glycol ethers
  - Tetrachloroethylene
  - Trichloroethylene
  - Vinyl chloride
  - Polyesters

- Butadiene
  - Adiponitrile
  - Rubber polymers

- Petroleum
  - Benzene
    - Cumene
    - Cyclohexane
    - Nitrobenzene
    - Alkyl benzene
    - Chlorobenzene
    - Adipic acid
    - Caprolactam
    - Aniline
    - Detergents and polymers
    - Nylon
    - Methylene diphenyl diisocyanate

- Toluene
  - Toluene diisocyanate
  - Benzoic acid
  - Xylene
  - Propylene
    - Isophthalic acid
    - Dimethyl terephthalate
    - Terephthalic acid
    - Polyurethane

- Xylene
  - Phthalic anhydride

- By-products
  - 44%
  - 26%

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Ethylene Derivatives

- **Polyethylene**
- Ethylene glycol
- Glycol ethers
- Ethoxylates
- Polyesters
- **Tetrachloroethylene**
- Trichloroethylene
- Vinyl chloride
- Polyvinyl chloride

Ethylene: 60%

Approximately 44% of petrochemical feedstock
Industrial Petrochemical Processes

- Ethylene
  - Polyethylene
  - Ethylene oxide
  - Ethanol
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- Nitrobenzene
- Aniline
- Methylene diphenyl diisocyanate
- Detergents and polymers
- Adipic acid
- Caprolactam
- Nylon
- Phenol
- Acetone
- Bisphenol A
- Polyol
- Polyethylene glycol
- Glycol ethers
- Acrylonitrile
- Polypropylene
- Propylene oxide
- Polypropylene
- Acrylic acid
- Allyl chloride
- Acrylic polymers
- Epichlorohydrin
- Isopropyl alcohol
- Xylene
- Toluene diisocyanate
- Benzoic acid
- Isophthalic acid
- Dimethyl terephthalate
- Terephthalic acid
- Phthalic anhydride
- Benzenes
- Toluene
- Xylene
- By-products

Law, P.K., Britton, T.J. Encyclopedia of Occupational Health and Safety
Targeting high potential processes

Cost of Electricity

Nylon 6,6

Hydrolysis

Adiponitrile

Adipic acid

Hydrogenation

Nylon 6,6

Hexamethylenediamine

Adiponitrile: Nylon 6,6’s key precursor
Importance of the electrochemical route

>500K tons/year

Electro Hydrodimerization

Acrylonitrile → Adiponitrile

Manuel M. Baizer
Monsanto, 1963

Electrohydrodimerization of AN to ADN

**Overall reaction**

\[ 2 \text{AN} + 2 \text{H}_2\text{O} + 2 \text{e}^- \rightarrow 2 \text{OH}^- + \text{ADN} + \frac{1}{2} \text{O}_2 \]

**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

**Cathodic reactions**

\[ 2 \text{H}_2\text{O} + 2 \text{e}^- \rightarrow \text{H}_2 + 2 \text{OH}^- \]

**Anodic reactions**

\[ 2 \text{OH}^- \rightarrow \text{H}_2\text{O} + \frac{1}{2} \text{O}_2 + 2 \text{e}^- \]
Desired and undesired reactions

Desired reaction:

AN → AN$^-$ → ADN$^+$ → ADN

2H$_2$O → e$^-$

Undesired reaction:

Na$^+$[PO$_4$]$_3$O$^-$ [PO$_4$]_2Na$^+$

Supporting electrolyte: Na$^+$[PO$_4$]$_3$O$^-$ [PO$_4$]_2Na$^+$

Chelating agent:

Anodic reactions:

2OH$^-$ → H$_2$O + 1/2 O$_2$ + 2 e$^-$

Cathodic reactions:

2H$_2$O + 2 e$^-$ → H$_2$ + 2 OH$^-$
Desired and undesired reactions

Cathodic reactions

Anodic reactions

Tetraalkylammonium ions (TAA ions)

Supporting electrolyte

Chelating agent

Desired reaction

Undesired reaction

- Desired reaction: $\text{AN} \rightarrow \text{AN}^- \rightarrow \text{ADN}^- \rightarrow \text{ADN}$

- Undesired reaction: $\text{AN} \rightarrow \text{PN}$

Chelating agent: $\text{N}^\circ - \text{C} - \text{N}^- - \text{O}\text{PO}_3\text{O}^- - \text{O}^- \text{Na}^+$

Supporting electrolyte: $\text{Na}^+ - \text{O}^- \text{P} - \text{O}^- \text{Na}^+$

Anodic reactions:

$2 \text{H}_2\text{O} \rightarrow 2\text{H}_2 + 2\text{O}_2 + 4\text{e}^-$
**Desired and undesired reactions**

**Cathodic reactions**

- **AN** → **AN⁻**
- **H₂O** + **AN** → **ADN⁻**
- **H₂O** → **PN**

**Supporting electrolyte**

- **Na⁺ - O⁻P⁻O⁻Na⁺**

**Chelating agent**

- **HO - N⁻ - C - O - Na⁺**

**Tetraalkylammonium ions (TAA ions)**

**Anodic reactions**

- **2 H₂O** → **2 H₂ + 2 e⁻**
- **2 OH⁻ → H₂O + 1/2 O₂ + 2 e⁻**

**Intermediate – basic pH**

- **pH 7-11**
83% selectivity towards ADN at -26 mA cm$^{-2}$

0.6 M AN
0.5 M Na$_3$PO$_4$
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

\[ t_c = 100 \text{ ms} \]
\[ t_r = 50 \text{ ms} \]
\[ t_r = 5 \text{ ms} \]

DC operation

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

ADN production

Longer reaction times increase AN conversion and ADN production

20% net increase in ADN production

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

80% decrease in PN production
Mitigation of mass transport limitations

Effect of cathodic and resting times

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

$250\%$ improvement in ADN:PN ratio

Blanco et al., *PNAS*, 2019, **116**, 17683-17689.
Data-driven Optimization
Functioning of Artificial Neural Networks

- Input layer
- Hidden layers
- Output layer

Variables:
- $t_c$
- $t_r$

ADN production
Functioning of Artificial Neural Networks
ANN-predicted ADN production

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

20% increase
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

Chemical reactions and models

ANN-predicted maximum region
Engineering Electrochemical Manufacturing

- **Reaction Development**
  - Electrosynthesis Discovery
  - Mechanistic Understanding
  - Electrocatalyst Development

- **Electrolyte Engineering**
  - Electrolyte Formulation
  - Ionomer Design
  - In-operando EDL

- **Operational Control**
  - Transport Phenomena and Kinetics
  - Reaction Engineering & Reactor Design

- **Data Analytics**
  - Machine Learning (aka statistics)
  - Automation & Control
  - Mixed Data/Modeling

**Multiscale Theory and Simulations / Characterization**
Electrochemical Reaction Engineering Toolkit

- Reaction discovery
- Environment Control
- Reactor engineering
- Prototyping and Scale-up

Microfluidics

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

http://dev.noram-eng.com/electrochemical/
Planning an Electrifying Engineering Research Center

Center for the Electrification of the Chemical Industry (CECI)

Thermochemical Plant (Outdated state-of-the-art)

- Exothermic Reactor
- Endothermic Reactor
- Feedstocks
- Coal
- Steam
- Water
- Pure Products
- Impure Products

Electrochemical Plant (CECI-Enabled Future)

- Electrolytic Reactor
- Galvanic Reactor
- Impure Oxidation Products
- Charged Energy Carriers
- Impure Reduction Products
- Discharged Energy Carriers
- Pure Products
- Renewable Electricity as Power Source

Fossil-Fuel Derived Heat as Power Source
Building an ERC from the ground up: Participate!

### Calling Teams in the Following Areas:

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### Timeline

- **Ideation**
  - Team Proposals (03/2020)
- **Convergence**
  - Workshop (05/2020)
- **Organization**
  - Team Selection (06/2020)
  - Team Meeting (08/2020)
- **Proposal Preparation**
  - Pre-proposal draft (10/2020)

[wp.nyu.edu/ceci](wp.nyu.edu/ceci)

[Images of Eray Aydil, Yury Dvorkin, Sanat Kumar, Miguel Modestino]
Thank you

www.modestinogroup.com

**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

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