U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

BIOENERGY TECHNOLOGIES OFFICE

BIOPROCESSING SEPARATIONS CONSORTIUM

Task 2.5: Electrochemical Separation Technologies to Extract Intermediate Organic Compounds

Separations Consortium Peer Review

Performance-Advantaged Bioproducts and Bioprocessing Separations

April 6, 2023

Yupo Lin and Lauren Valentino
(ANL)

Argonne NATIONAL LABORATORY | BERKELEY LAB | Los Alamos NATIONAL LABORATORY | NREL NATIONAL RENEWABLE ENERGY LABORATORY | OAK RIDGE National Laboratory | Pacific Northwest NATIONAL LABORATORY

Bioprocessing Separations Challenge

BETO Conversion barrier and challenge

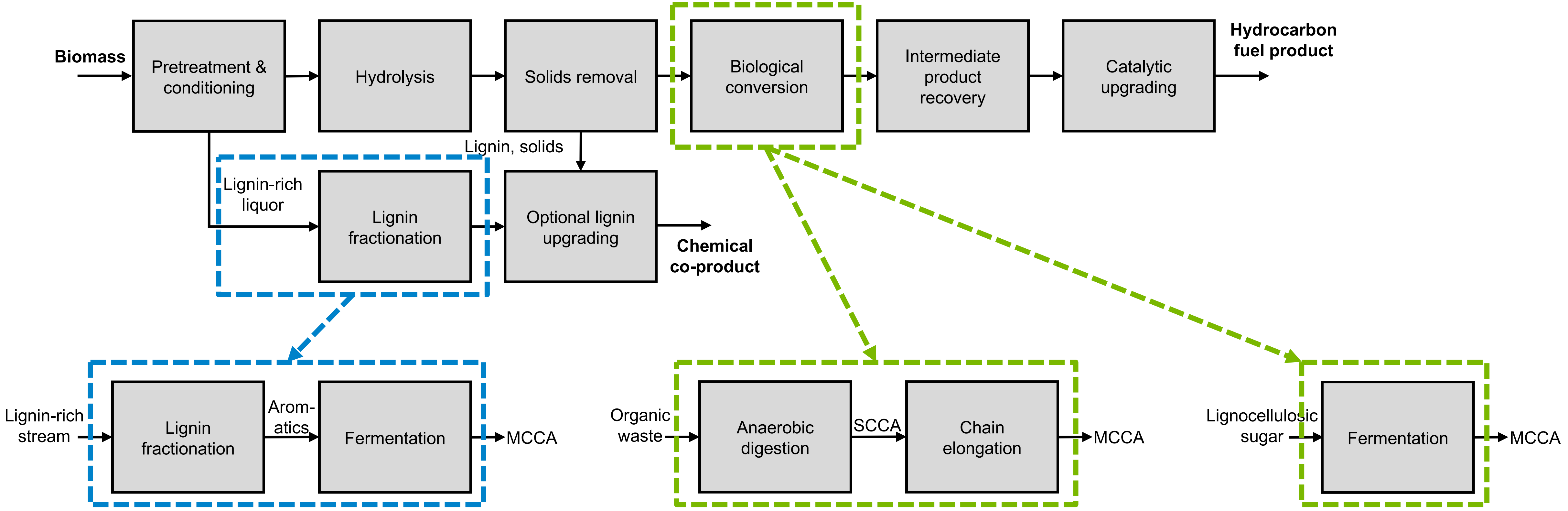
Separation of **organic species** in biomass processes for upgrading to final fuel and bioproduct molecules has high energy requirements. **Low-cost** purification technologies need to be developed to remove other organic contaminants and provide **concentrated, clean intermediates** from which **biofuels and bio-based chemicals** can be manufactured.

Bio-Based Medium Chain Carboxylic Acids (MCCA)

- Volatile fatty acids are not suitable as fuel because of their high oxygen-to-carbon ratio and energy density (870 – 2,800 KJ/mol)
- Previous work in the Consortium focused on electrochemical separation technologies (ESTs; electrodeionization, electrodialysis, and capacitive deionization) for short chain carboxylic acids (SCCAs) but further upgrading to high-energy and easily separable products is needed
- C5-C12 carboxylic acids
- Higher energy density (3,500 - 4,800 KJ/mol) due to lower oxygen/carbon ratios
- Used for production of sustainable aviation fuels, direct replacement chemicals, and performance-advantaged bioproducts
- Production routes
  - Fermentation of lignocellulosic sugar or lignin-derived aromatics
  - Chain elongation of short chain carboxylic acids

Bio-Based Medium Chain Carboxylic Acids

Dry Feedstocks to Fuels via Low-Temperature Conversion



Bioprocessing Separations Challenge

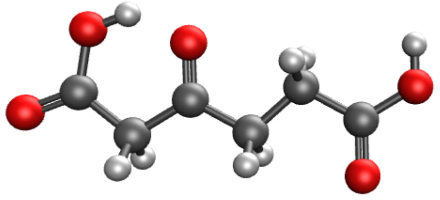
Project goal

- Separate and recover medium chain carboxylic acids acids from bioconversion streams for SAF and/or biochemical production to support BETO goals for decarbonization of transportation and industry
  - β-ketoadipic acid, muconic acid, and aconitic acid are target products in BETO's Agile BioFoundry
  - Mevalolactone (exists in equilibrium with mevalonic acid) is the target product of industry partner Visolis

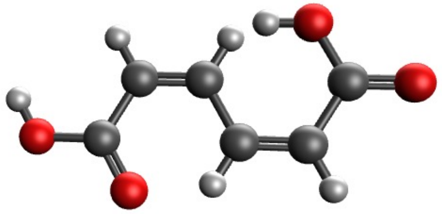
Agile BioFoundry

VISOLIS

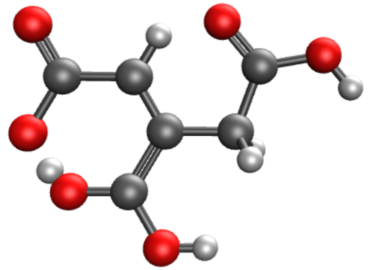
β-ketoadipic acid



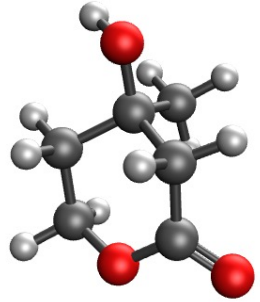
Muconic acid



Aconitic acid



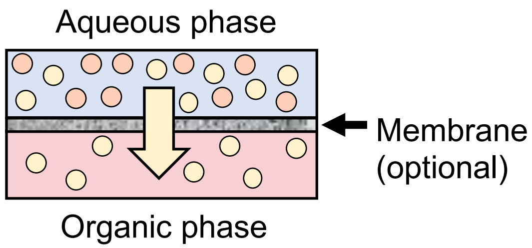
Mevalonolactone



State of Technology

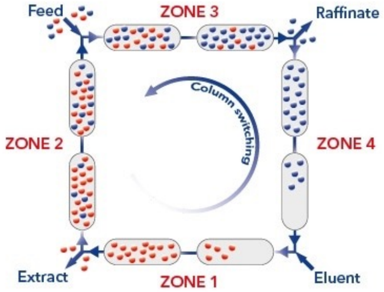
Liquid-liquid extraction

- Limited to narrow pH range
- Limited to acids with boiling point <240°C
- Solvent recycling requires additional separation step



Simulated moving bed (SMB)

- Limited to 2-component separations
- Expensive stationary phase
- Strong acid and base required to protonate acid and regenerate SMB

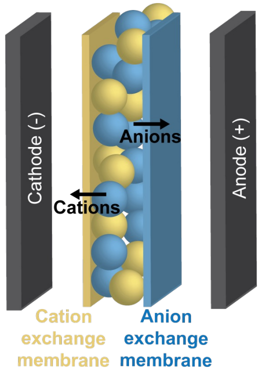


Thermal processes

- Energy and cost intensive

Electrodialysis/electrodeionization (previous funded for SCCA)

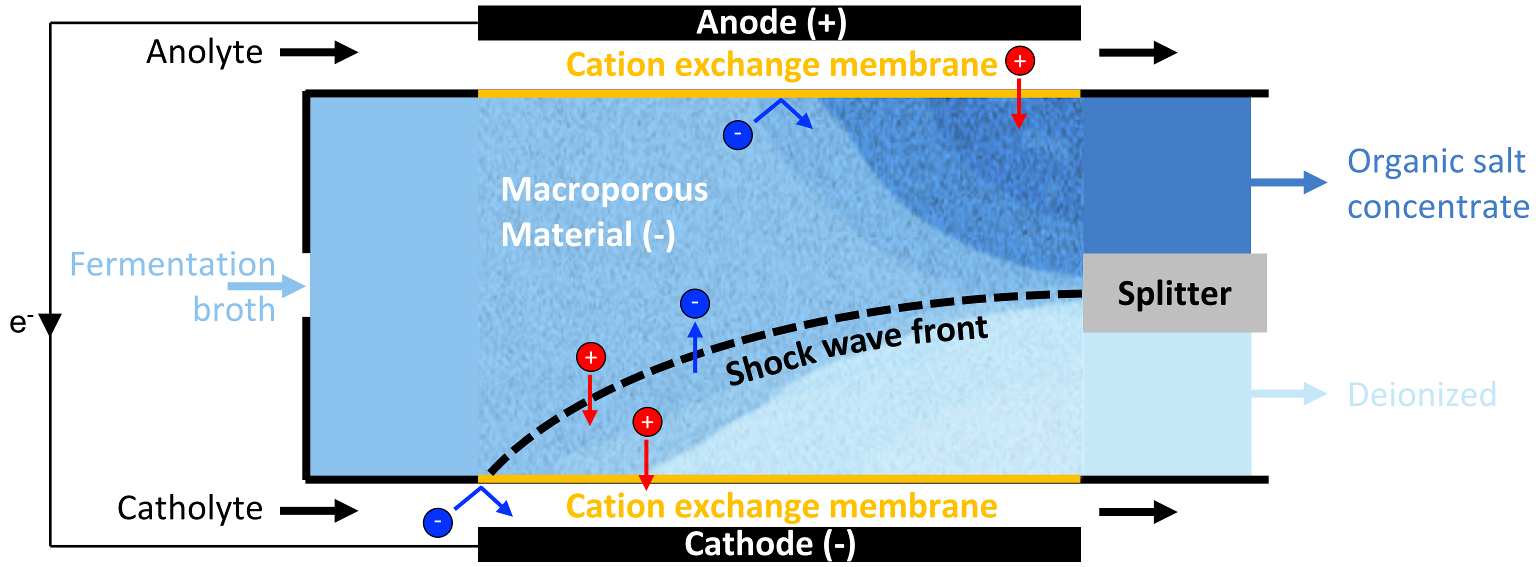
- Anion exchange membrane (AEM) fouling by highly hydrophobic C_5-C_{12}
- High energy consumption due to limited transport to cross AEM for large, hydrophobic organic molecules



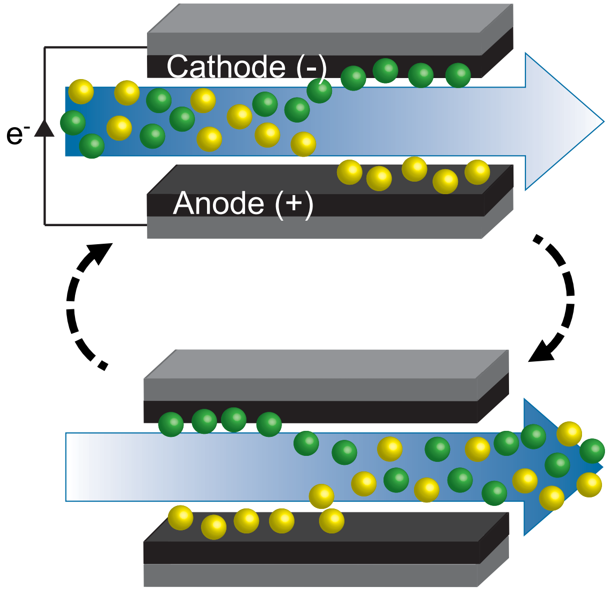
Approach: Electrochemical Separations

Develop, scale-up, and demonstrate electrochemical separation technologies that **eliminate the use of anion exchange membranes**, thereby, eliminating membrane organic fouling and overcoming mass transport limitations - **challenges for industrial application indicated by IAB**

Shockwave electrodeionization (SWE)



Capacitive deionization (CDI)



Approach: Electrochemical Separations

Shockwave electrodeionization (SWE)

- New electrochemical separations platform that will leverage learnings from previous work on other electrochemical separations for SCCA and MCCA separations
- Utilize microfluidic separation design to overcome MCCA transport limitations
- Target organic ion separations

Capacitive deionization (CDI)

- Continuation of the process development in FY20-22 using a bench-scale CDI system for SCAA
- Build on FY22 demonstration that custom-built software and hardware work in conjunction to spatially separate the deionized and concentrated streams, not normally achieved in the CDI SOT
- Scale by 10x and further improve by modifying operating parameters and/or cell design to increase throughput and operate using real bioprocessing streams
- Target inorganic ions

ESTs have been shown to have low carbon and water footprints in prior SepCon R&D projects

Both SWE and CDI eliminate the use of anion exchange membranes → eliminate membrane fouling

Approach: Metrics and Risks

Technical approach

- Parallel development of SWE and CDI processes
- Sequential integration into biochemical conversion process

Technical, economic, and sustainability metrics

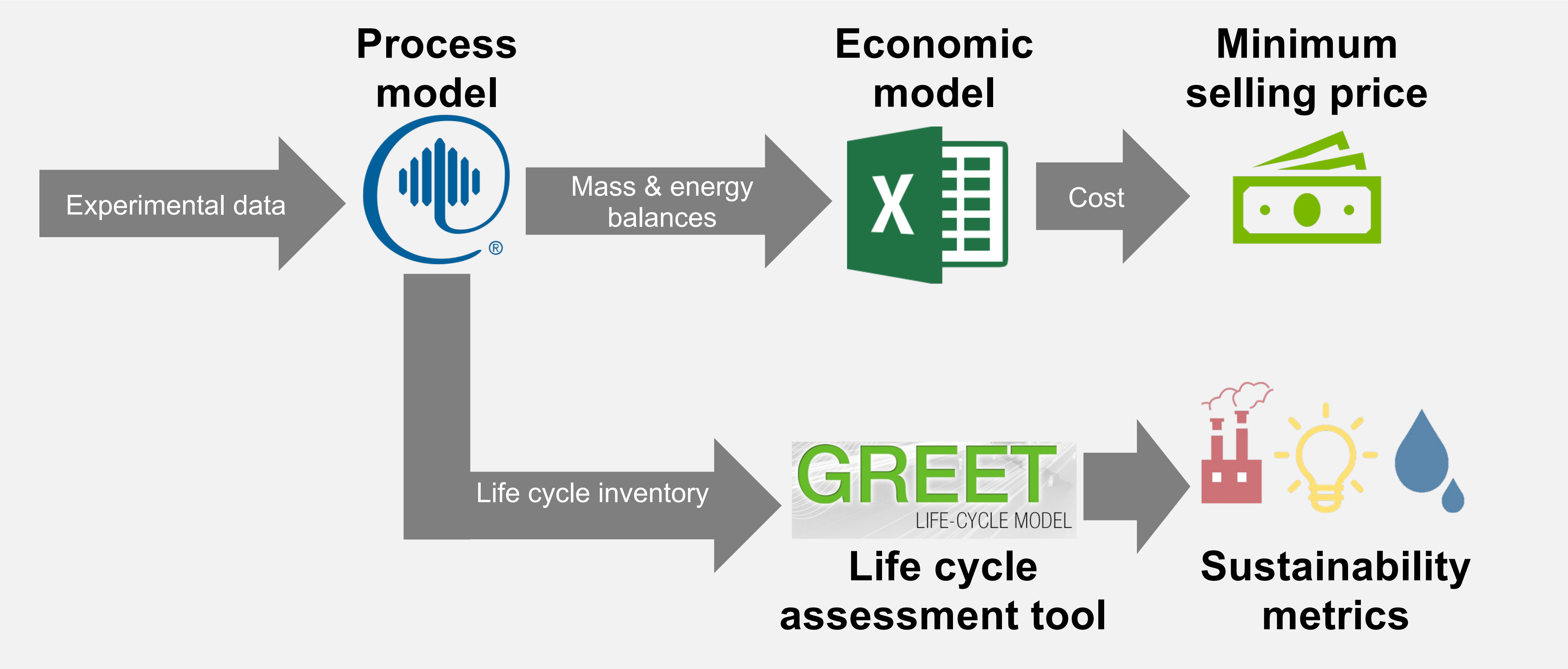
- Energy consumption, recovery, and purity
- Minimum selling price
- Greenhouse gas emissions, energy consumption, and water consumption

Risks

- Poor flow distribution in a porous matrix is detrimental to separation productivity but can be mitigated by optimizing device fabrication with in-situ flow distributor. Uniform pore distribution can be adjusted during material manufacturing and verified by a non-destructive testing system.
- Organic fouling on the adsorbent material may occur but can be mitigated through clean-in-place and/or pretreatment.

	Technical metrics		**Economic and sustainability metrics**
Year	**Shockwave electrodeionization (SWE)**	**Capacitive deionization (CDI)**	
1	30% acid capture, SCCA	<300 ppm inorganics	-
2	50% acid capture, <2 kWh/lb MCCA	Scale from 14 cm^2 to 200 cm^2	Analysis for each unit operation
3	80% acid capture <1 kWh/lb MCCA, <100 ppm inorganics from a fermentation broth		50% reduction in energy consumption compared to baseline separations for TEA and LCA

Approach: Integrated Analysis



GREET[TM]: Greenhouse gases, Regulated Emissions and Energy use in Transportation

Approach: Management

- Progress tracking with monthly Consortium meetings
- Weekly analysis meetings to evaluate economic and sustainability measures
- Ad hoc inter-lab meetings to coordinate milestones and deliverables
- Findings published and IP generated for new concepts
- Bi-annual meeting with Industrial Advisory Board for progress updates and feedback
- Collaborate with other BETO projects and industry partners
  - Agile BioFoundry
  - Visolis

Approach: Go/No-Go Decision

Name	Description	Criteria	Date
Task 2.5 EST to Extract Intermediate Organic Compounds [ANL]: Technical feasibility assessment of organic acid separations by shockwave electrodialysis (SWE)	Demonstrate technical feasibility of carboxylic acid capture using SWE, present SWE and CDI performance to the biomanufacturing industry, and obtain feedback from the biomanufacturing industry on the application of ESTs in industry.	Demonstrate 30% carboxylic acid capture and get industry feedback to support that ESTs are industrially relevant for post-fermentation product separation and recovery.	9/30/2023

Approach: Diversity, Equity, and Inclusion

Research team

- Diverse team including scientists and engineers from STEM underrepresented groups

FY22 outreach activities

- Introduce a Girl to Engineering Day
- Science Careers in Search of Women
- Helped develop Argonne's Educational Programs and Outreach March 2022 newsletter - includes an at home separations activity for students in grade 7+

FY22 student mentoring

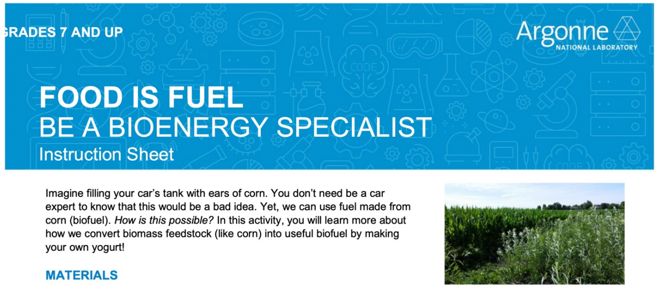
- 4 undergraduate student internships

Economic development

- Utilize vendor and procurement systems that support purchasing goods/services from veterans, women, and disadvantaged owned small businesses

FY23 Bioenergy Bridge to Career Program

- Researchers will participate in Consortium-wide program


RADES 7 AND UP

Argonne
NATIONAL LABORATORY

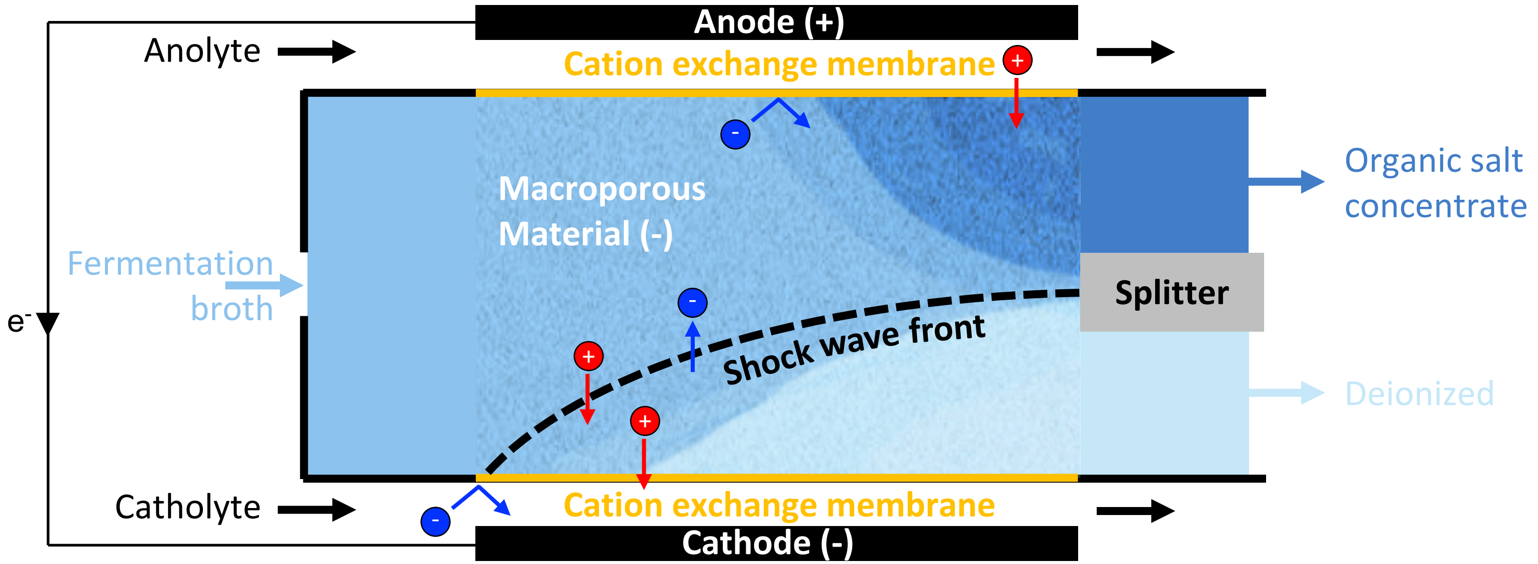
FOOD IS FUEL
BE A BIOENERGY SPECIALIST
Instruction Sheet

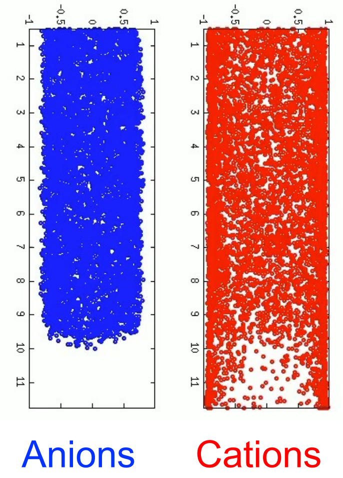
Imagine filling your car's tank with ears of corn. You don't need be a car expert to know that this would be a bad idea. Yet, we can use fuel made from corn (biofuel). *How is this possible?* In this activity, you will learn more about how we convert biomass feedstock (like corn) into useful biofuel by making your own yogurt!

MATERIALS

Shockwave Electrodeionization (SWE)

- Weakly negatively charged microporous material sandwiched between cation exchange membranes
- Apply electrical current exceeding diffusion-limited current to produce a deionization shock
- Cross-fed stream is split into concentrated and deionized products at the outlet
- Does not use anion exchange membranes
- Ionization and transport properties of weak organic acids will determine the separation efficiency and energy consumption

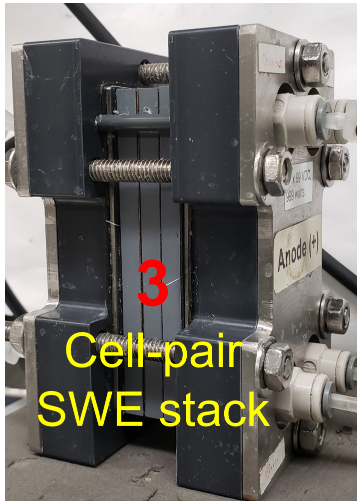




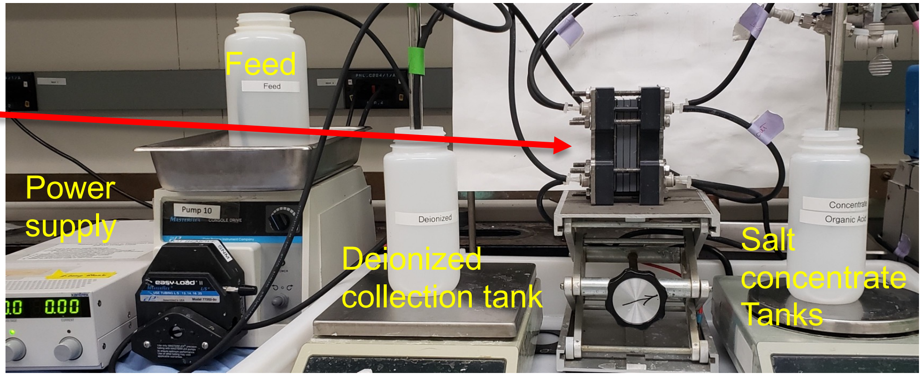
Mani and Bazant, *Physical Review E*, 2011

Progress and Outcomes: Scalable SWE Device Design, Implement & Test

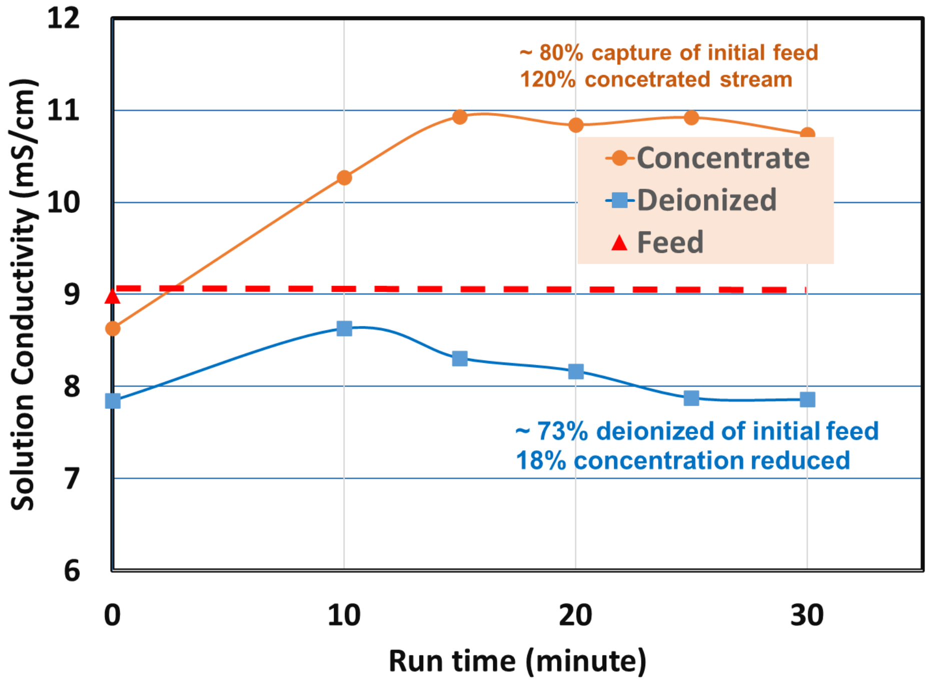
- Successfully designed, fabricated, implemented and operate a “Scalable” SWE stack
- Scoping test validates a successful operation of the scalable SWE stack



Prototype scalable SWE stack



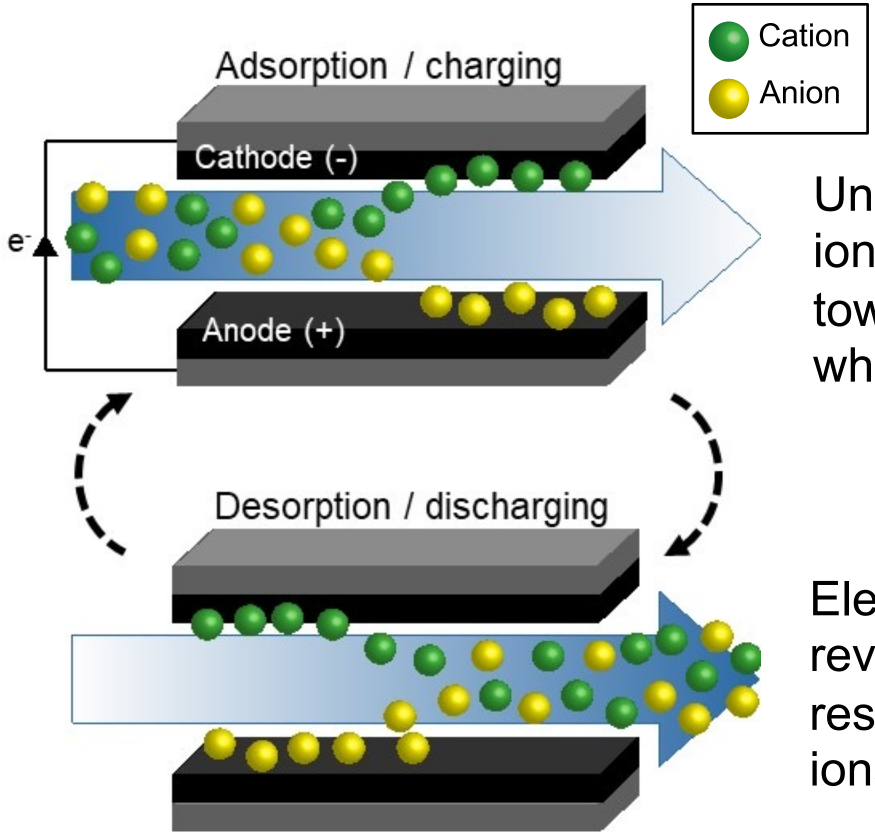
Once-through operation of a scalable SWE system



Separation of ionic solution into deionized and concentrate salt brine streams using the scalable SWE device

Future work – Investigate the impact of operation conditions and Porous resin wafer property on separation performance for process optimization.

Capacitive Deionization (CDI)



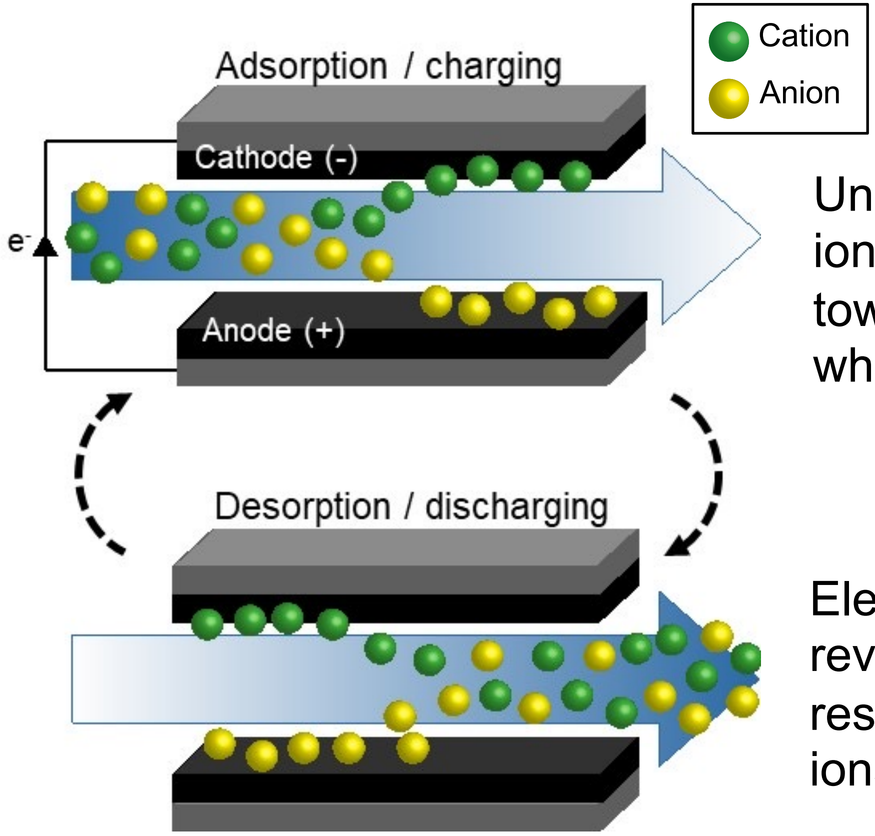
Under applied potential, ion transport is driven towards electrodes where ions are stored

Electric potential is reversed or removed resulting in release of ions

Advantages

- No phase transition
- No chemical reagents for regeneration
- Intrinsically reversible through modulating electric potential
- Targets and removes the minority component (ions) rather than the majority component (water)
- Relatively low energy consumption
- Tunable electrode materials and flexible operation strategies enable selective electrosorption of target ionic species

Progress and Outcomes: Reversible Electrosorption via Capacitive Deionization



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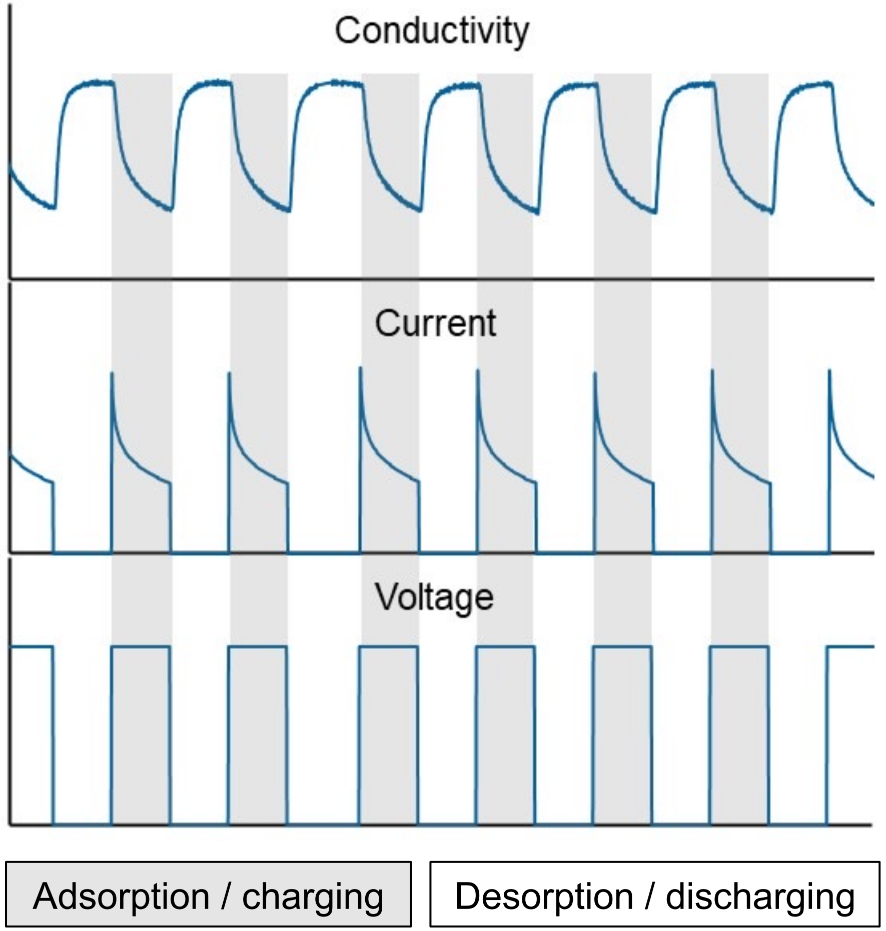
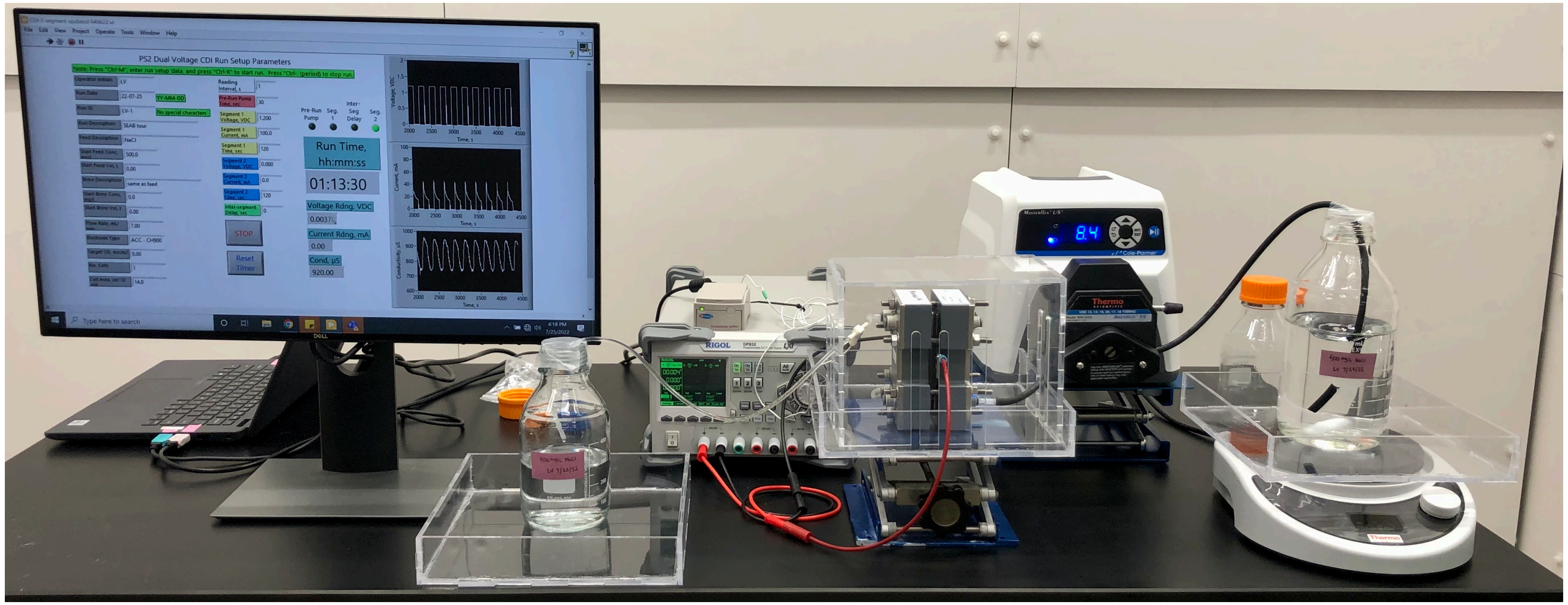


Consistent and reversible ion removal and recovery

Progress and Outcomes: Control and Data Logging Software

- Control applied electric field
- Control process input flow rate
- Synchronize changes in process variables
- Automated data acquisition of process voltage, current, and conductivity data
- Real-time data collection and display



Impact

Advances over other industrial separation technologies

- Eliminate fouling & transport resistance of anion exchange membranes
- More sustainable - lower GHG and water footprint

Outcomes

- Demonstrate technical feasibility, process scale-up, and performance of integrated TRL 4 electrochemical separation technologies
- Industry engagement will guide project deliverable (FY23 Q4 GNG)

Industrial application

- Biorefining - biochemicals and biofuels
- Energy and water supply - waste to energy, water reclamation/reuse

Industrial collaborations

- Waste to energy and CO_2 utilization partners will review technical performance

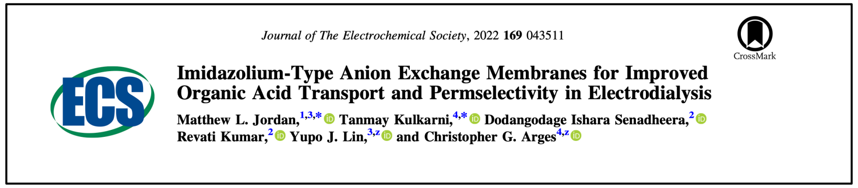
BETO collaboration

- Agile BioFoundry

Impact

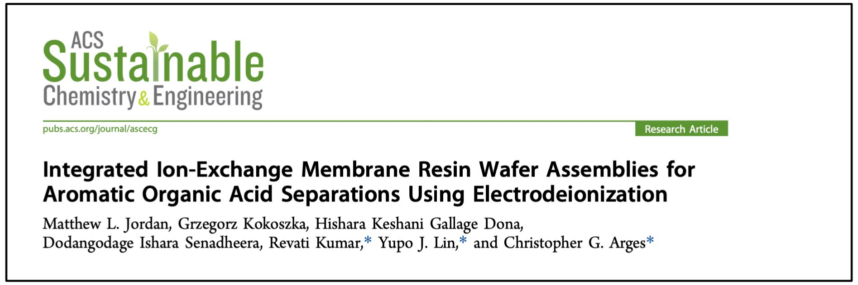
Publications

- Valentino *et al*. (2023), provisionally accepted for publication in *ACS Sustainable Chemistry & Engineering*
- Lin et al. (2023), *ACS Sustainable Chemistry & Engineering, January 11, 2023,*
- Lin et al. (2022), *Journal of The Electrochemical Society, Number 4, 2022.*


Journal of The Electrochemical Society, 2022 **169** 043511

Imidazolium-Type Anion Exchange Membranes for Improved Organic Acid Transport and Permselectivity in Electrodialysis

Matthew L. Jordan,[1,3,*] Tanmay Kulkarni,[4,*] Dodangodage Ishara Senadheera,[2] Revati Kumar,[2] Yupo J. Lin,[3,z] and Christopher G. Arges[4,z]


pubs.acs.org/journal/ascecg | Research Article

Integrated Ion-Exchange Membrane Resin Wafer Assemblies for Aromatic Organic Acid Separations Using Electrodeionization

Matthew L. Jordan, Grzegorz Kokoszka, Hishara Keshani Gallage Dona, Dodangodage Ishara Senadheera, Revati Kumar,* Yupo J. Lin,* and Christopher G. Arges*

IP

- US patent application #17/699,339, Membrane-wafer assembly for electrodeionization, 03/2022
- US patent application ## 17/137,956, System and method for biological methane gas generation and removal of carbon dioxide therefrom, 10/2021
- IN-21-141 Electrochemical Ion Extraction And Recovery

Summary

Approach	Development of shockwave electrodeionization and capacitive deionization processes in parallel Integrated TEA and LCA identify research and development priorities and guide experimental work Frequent interaction and coordination among researchers to meet project goals Regular updates and feedback from the Advisory Board
Progress and Outcomes	Successfully fabricated and implemented a prototype “scalable” SWE stack for separations Demonstrate technical feasibility of SWE performance to separate and concentrate ions from process stream Reversible electrosorption of ions was demonstrated using CDI based on scalable electrochemical cell designs Developed a customized CDI system integrated control and data logging software and successfully demonstrated that the software and hardware work in conjunction to spatially separate the deionized and concentrated streams
Impact	Knowledge and tools to enable commercial scale electrochemical separations for bioprocessing Shockwave electrodeionization and capacitive deionization technologies provide advances over other industrial separation technologies: ▪ Eliminate fouling & transport resistance of anion exchange membranes ▪ More sustainable - lower GHG and water footprint ▪ Provide a pathway for electrification, which is key to decarbonizing the economy Ongoing collaboration with industry and dissemination results via conference presentations and peer-reviewed journal articles enable technology transfer Industry engagement guides project deliverable (FY23 Q4 GNG)

Quad Chart Overview

Timeline

- Project start date: October 2022
- Project end date: September 2025

	FY22 Costed	FY23-25 Total Award
DOE Funding	$0	$1,200,000
Project Cost Share *	N/A	N/A

TRL at Project Start: 3
TRL at Project End: 4

Project Goal

The goal of this project is to conduct research towards the development and implementation of electrochemical separations technologies (EST) as a cost-effective and energy-efficient separations strategy to separate and purify MCCA for SAF.

End of Project Milestone

Develop a potential "game-change" new separations platform based on electrochemistry (SWE) for the selective separation of organic species.

Development a scalable (10x bench-scale) CDI process using real bioprocessing streams to evaluate economic feasibility and practical potential for using CDI to remove ionic impurities from bioprocessing streams.

Project Partners

- NREL, PNNL (TEA and Agile BioFoundry)
- Visolis (Industry partner)
- Renew CO_2 Inc. (Industry partner)

Acknowledgements

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BIOENERGY TECHNOLOGIES OFFICE

- Gayle Bentley
- Ben Simon
- Anthony Sorbera

BERKELEY LAB

OAK RIDGE National Laboratory

Argonne NATIONAL LABORATORY

- Airelle Alejandre
- Thomas Lippert
- Yuan Li
- Thathiana Benavides

NREL NATIONAL RENEWABLE ENERGY LABORATORY

- Eric Tan

Los Alamos NATIONAL LABORATORY

Pacific Northwest NATIONAL LABORATORY

Thank you!

Additional Slides

Responses to Previous Reviewers' Comments

- If your project has been peer reviewed previously, address 1-3 significant questions/criticisms from the previous reviewers' comments which you have since addressed
- Also provide highlights from any Go/No-Go Reviews

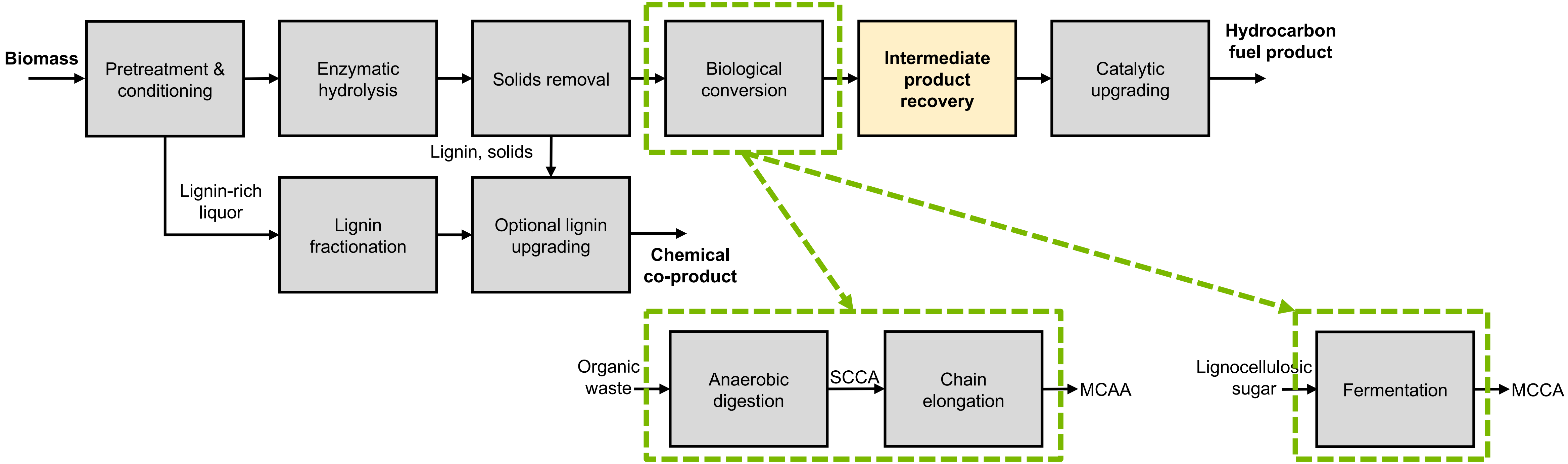
Note: This slide is for the use of the Peer Reviewers only – it is not to be presented as part of your oral presentation. These Additional Slides will be included in the copy of you presentation that will be made available to the Reviewers.

Presentations

- Yupo Lin, Novel Electrochemical Technologies for Sustainable Fuel/Chemical Production and Resources Recovery, Invited speaker at 242nd ECS Meeting, October 10, 2022
- Yupo Lin *et al.*, Resource Recovery from Solid Waste Anaerobic Digester Performance, Energy consumption and Cost, 2022 AICHE Fall Meeting
- Yupo Lin *et al.*, Membrane Separations to Capture Organic Acids and Valuable Co-product from Alkaline-Pretreated-Liquor of Lignin, 2022 ACS Fall Meeting
- Yupo Lin *et al*., Efficient resource recovery to enhance biomass conversion, 2021 AICHE Fall Meeting
- Valentino *et al.*, Reversible Electrosorption of Carboxylates for Bioenergy Production Through Capacitive Deionization, 2022 ACS Fall Meeting

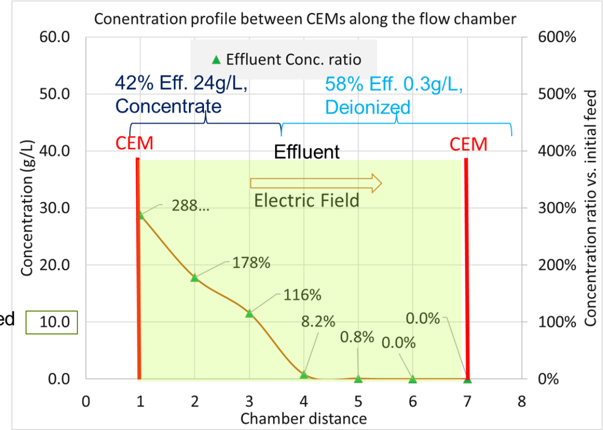
State of Technology: Electrodeionization

- Organic acid separation by resin wafer electrodeionization (RW-EDI) has been demonstrated to have low carbon and water footprints and to be cost-effective to capture short chain carboxylic acids[1,2]
  - Energy consumption: ~8x higher for medium chain vs. short chain carboxylic acids
  - Separation ratio: low for medium chain (35% for p-coumaric acid) vs. short chain (96% for lactic acid)

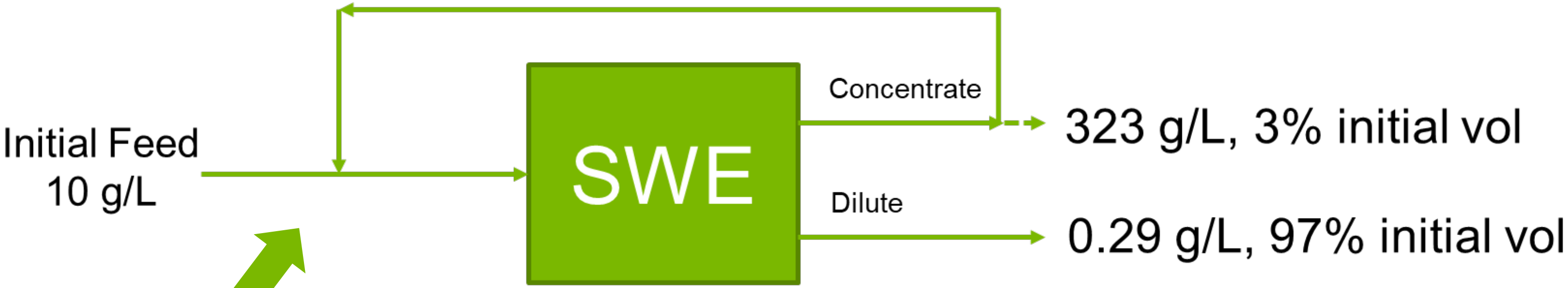


1) Jones et al. Bioprocessing Separations Consortium Three-Year Overview, 2020
2) Karp *et al., Lignin Rich Stream Fractionation and Purification,* BETO Peer Review 2021

Progress and Outcomes: Simulated Operation of SWE for Organic Acid Separation

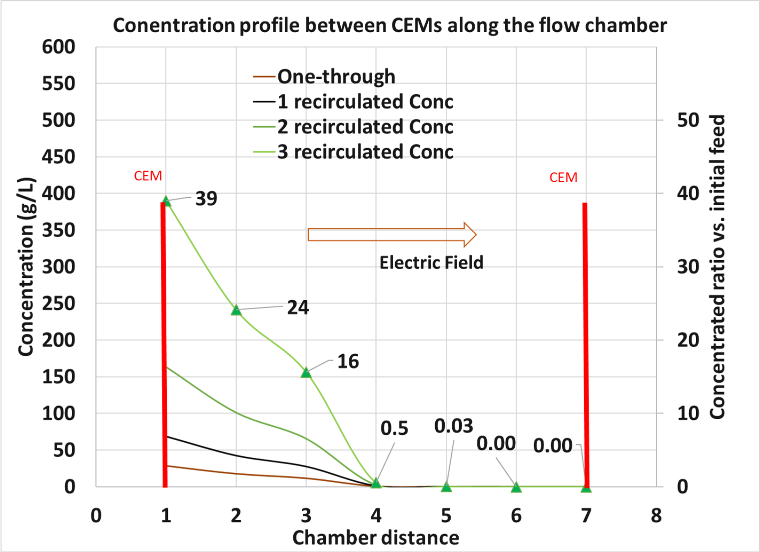


Concentration profile after initial, single pass operation



Total 4 operations of recirculated concentrate salt stream

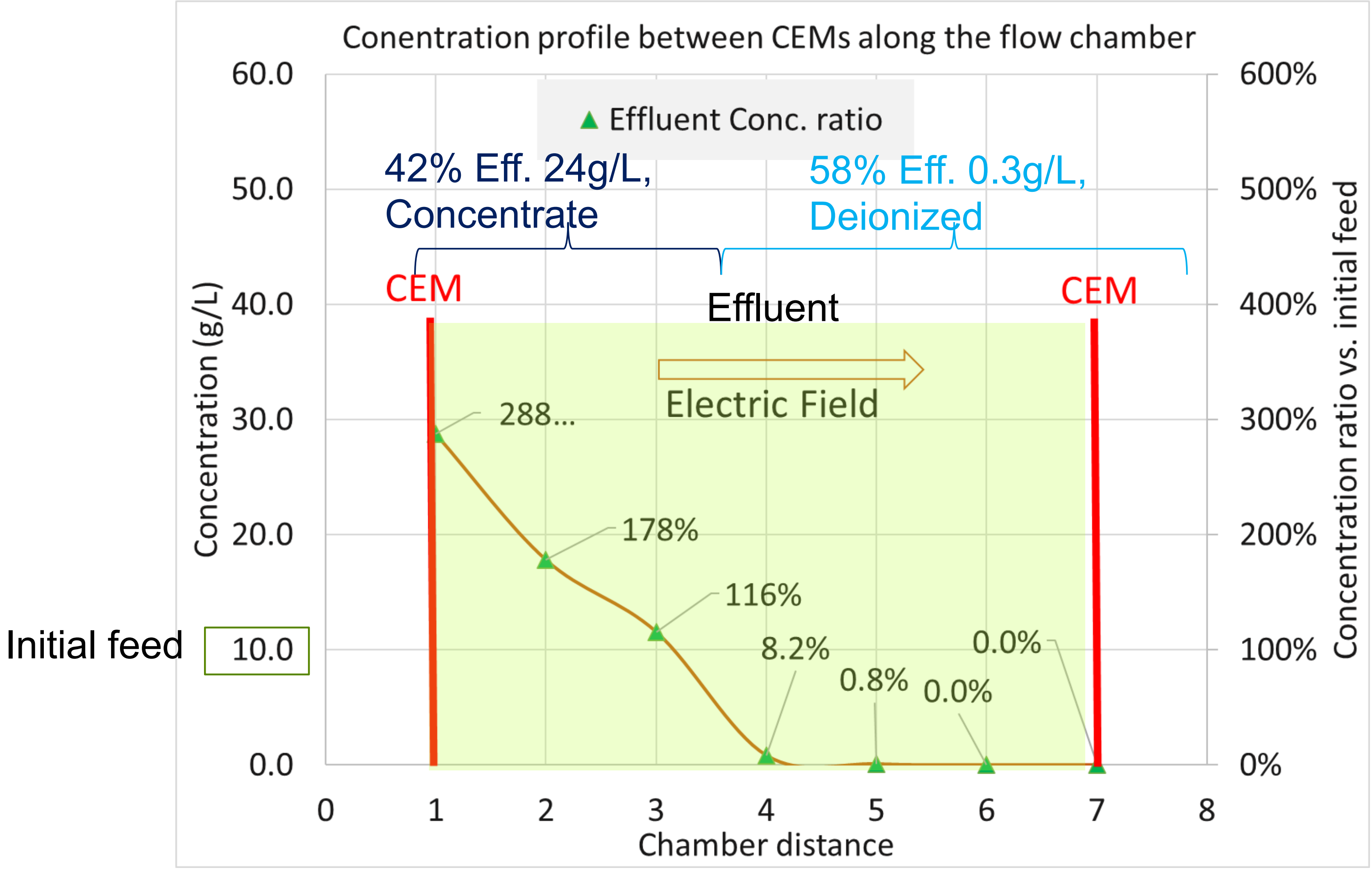
Estimated energy consumption ~ 0.48 kWh/kg salt



Concentration profile after multiple passes operation

Number of recirculation	Concentration (g/L)			Volume Uptake by Dilute (%)	
	Feed	Conc.	Dilute	one pass	Total
0	10	24	0.1	58%	58%
1	24	57	0.3	58%	83%
2	57	135	0.7	58%	93%
3	135	323	1.6	58%	97%
Final concentation		**323**	**0.29**		
Total Vol vs. Feed		**3%**	**97%**		
Total Capture Ratio		**97%**			

Shockwave Electrodeionization (SWE)

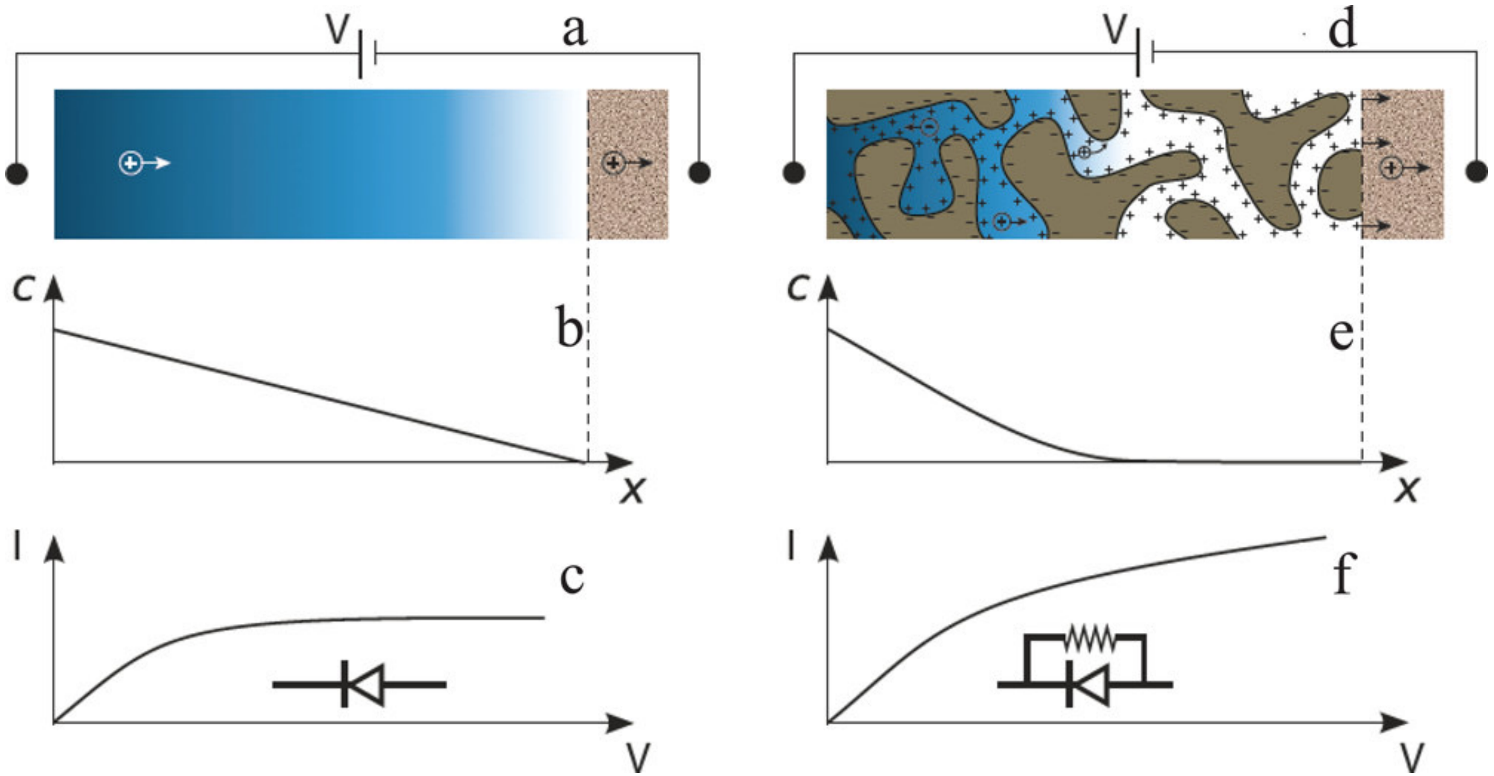


Preliminary Analysis of Shockwave Electrodeionization (SWE)

	Parameters/results for NaCl desalination, reported by MIT				Estimated for organic acid capture
Flow rate (mL/min)	0.06	0.06	0.038	0.076	**0.532**
Membrane area (cm2)	2				**14**
Thickness (mm)	8	8	2.76	2.76	
Concentration (mg/L)	585	585	585	5,850	**9,000**
Separation ratio (total salt, %)	99	60	99	95	**90**
Water recovery	50	50	80	65	**80**
Productivity (desalting, g/m2/h)	3	2	3	77	**148**
Applied potential (V)	1.5				**5**
50% current efficiency (A)	0.001	0.001	0.001	0.016	**0.009**
Energy (W)	0.001	0.001	0.001	0.024	**0.43**
Estimated energy consumption (kWh/kg)	0.04	0.06	0.04	0.03	**0.03**
Estimated energy consumption (kWh/ton)	0.4	0.4	0.6	5.2	**13.4**

>70% potential reduction in energy consumption for organic acid separation (0.10 vs. 0.5 kWh/lb)
80% reduction of water content with 5-fold increase of the capture acid titer
~50% reduction of capital footprint compared to RW-EDI technology

Impact of Porous Charged Matrix in SWE



Steady ion concentration polarization from a reservoir to an ideal cation-selective membrane through a bulk electrolyte (a), where the salt vanishes at the membranes (b) at the diffusion-limited current (c) analogous to the diode or through a negatively charged porous medium with thin double layers (d), where surface transport enables a broad depleted region (e) and a nearly constant overlimiting conductance (f), acting as a shunt resistance

Progress and Outcomes: Control and Data Logging Software