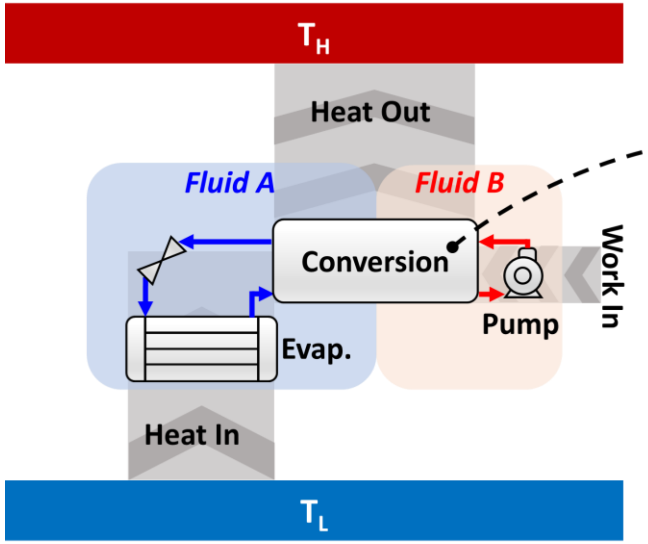
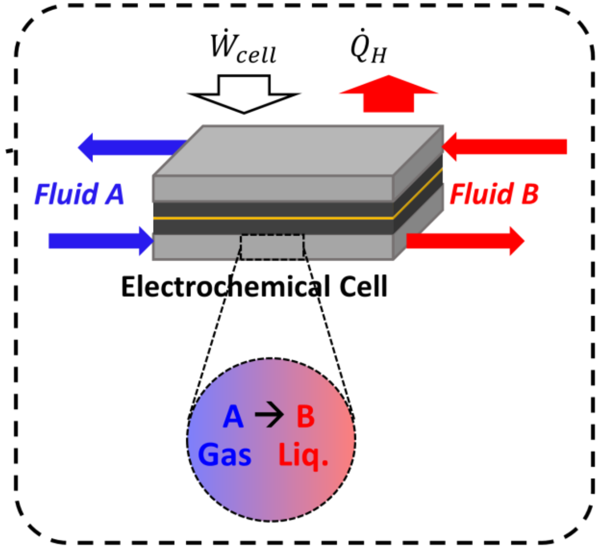
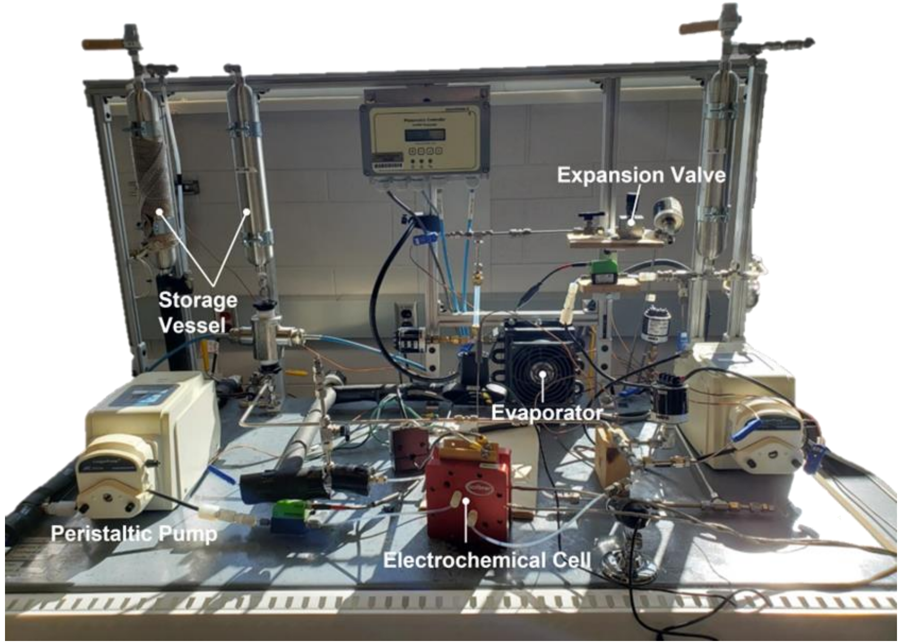
No Vapor-compression, Electrochemical-Looping Heat Pump (NOVEL HP)







Ray W. Herrick Laboratories, Purdue University; University of Illinois Urbana-Champaign (UIUC); Carrier Corporation
Lead PI: Davide Ziviani, Assistant Professor of Mechanical Engineering, Associate Director of CHPB
PI email: dziviani@purdue.edu

Award Number: DE-EE0008673

Project Summary

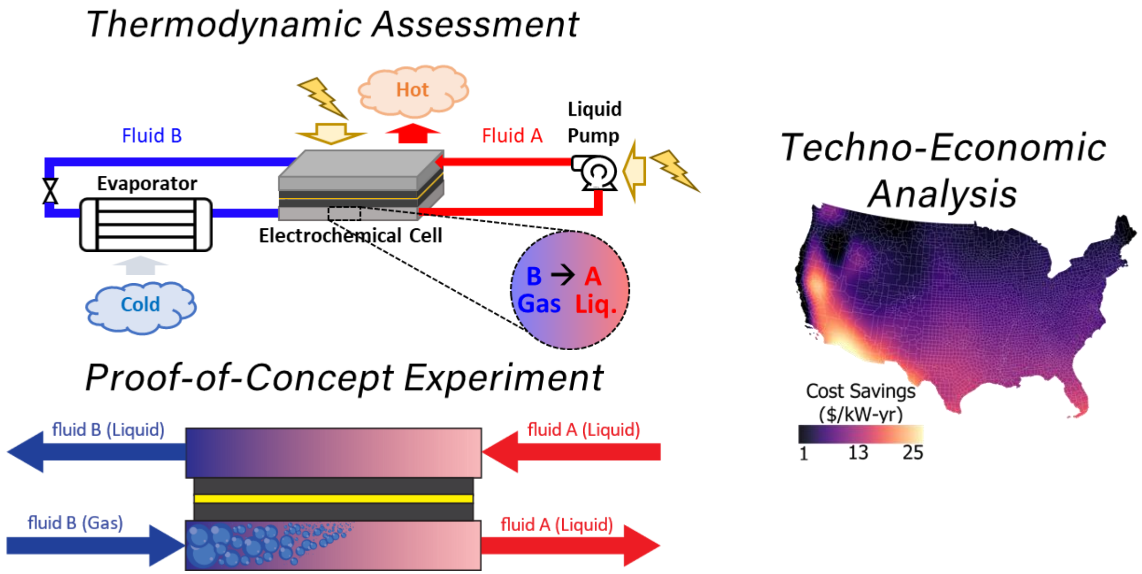
Objective and outcome

The overarching goal of this project is to **accelerate the development of electrochemical looping heat pump (ELHP) technology**, which has the potential to outperform conventional vapor compression systems.

Two major components are investigated:

- *New electrochemically active working fluids*
- *High performance cells*

The final project outcome shall be a TRL-3/4 demonstration of a down-selected ELHP system architecture



Team and Partners

Members: 4 faculty (3 ME; 1 Chem.E.); 3 PhD students (1 Purdue; 2 UIUC); 1 Post-doc (Purdue).

Past Members: Junyoung Kim (PhD Purdue, Dec 2022), Post-doc at NREL; Abhiroop Mishra (PhD student, UIUC), Link Fellowship

Industrial Partner: Carrier Corporation

Stats

Performance Period: **June 1, 2019 (effective Dec 1, 2020) till Nov 30, 2023**

DOE budget: **$999.8k**, Cost Share: **$283.6k**

G/NG-1 [Completed]: COP improvement of >20% over VC cycles and the projected capital cost of this system enables a simple payback of ≤ 3 years

G/NG-2: Demonstrate > 0.1 A/cm2 **[Completed]** at voltage efficiency ≥ 60% **[Ongoing: Achieved ~30%]** with at least one EWF

Problem

Building Energy Consumption:

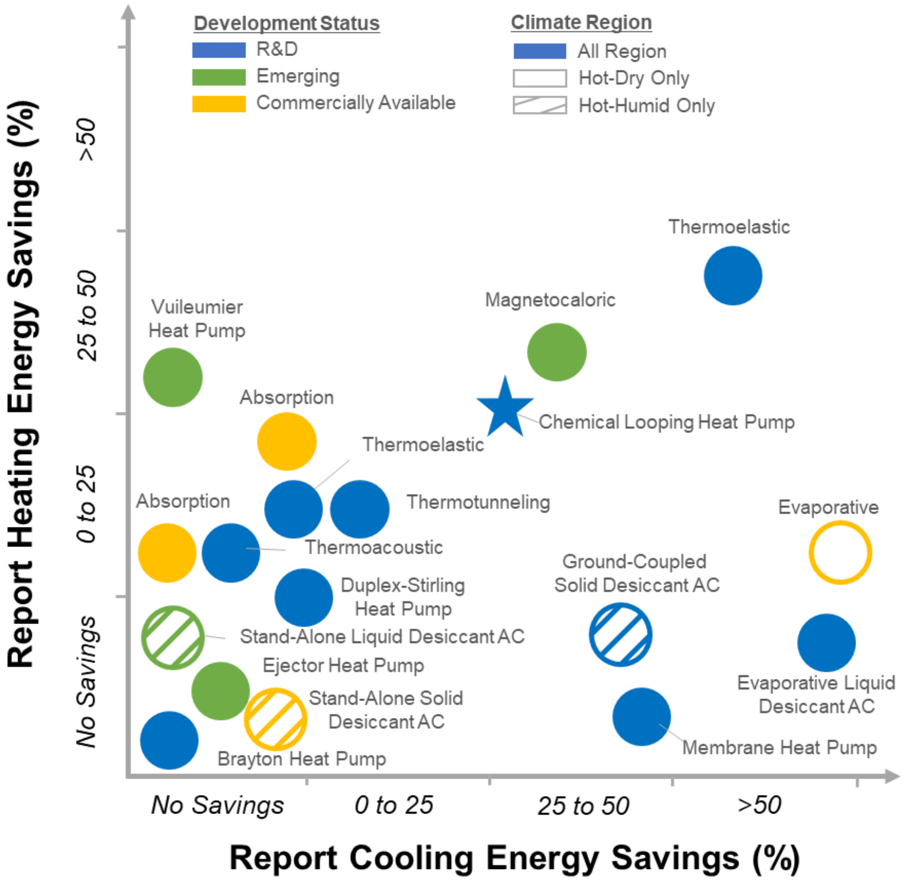
- 40% (40 quads) of the nation's primary energy demand in residential and commercial buildings in the U.S.
- 30~40% of energy for space cooling, heating, and refrigeration
- Indirect CO2 emissions ~1.6 $GtCO_2eq$ (IEA, 2021)
- Conventional HVAC&R Technologies employ high GWP refrigerants that contribute to global warming

DOE long term goals:

- 85% reduction in HFCs by 2035 and transition to low-GWP/natural refrigerants
- Alternative HVAC&R technologies

Next Generation HVAC&R:

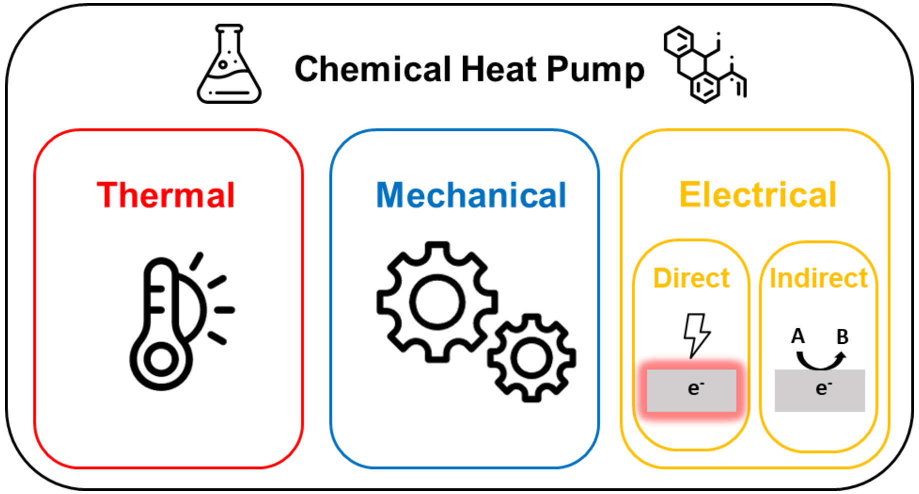
- *Cost and energy-efficient non-vapor compression system*
- *20~30% energy saving of electrochemical heat pumps*
- *Potential scalable technologies w.r.t. solid-state systems*

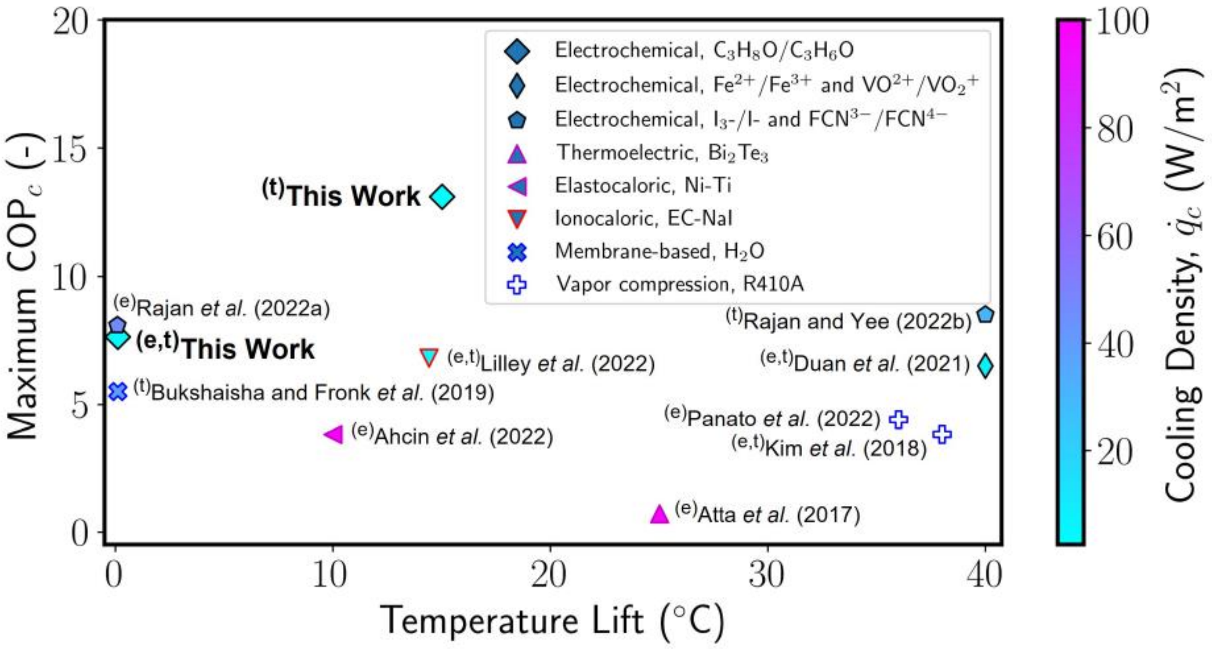


Updated from U.S. DOE EERE BTO (2014)

Alignment and Impact

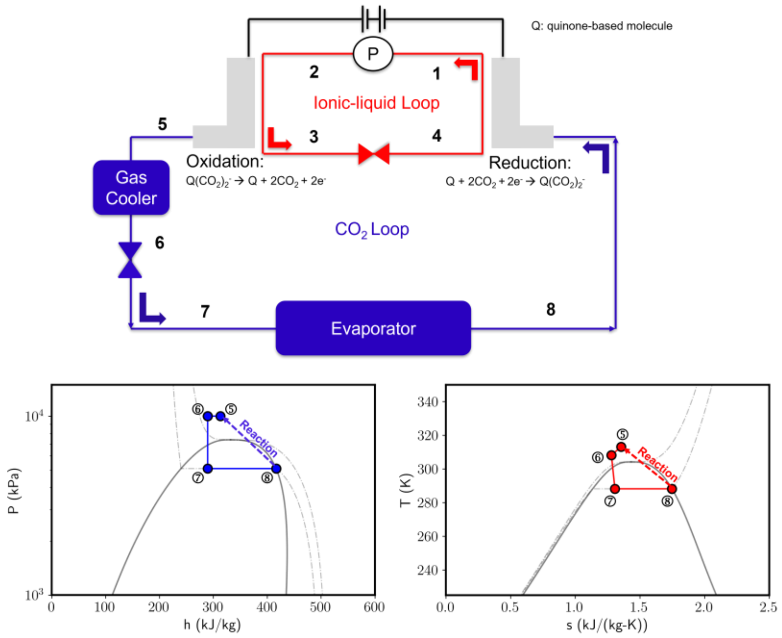
- Evaluate Alternative HVAC&R Technologies to Enable Electrification and Energy Savings:
  - Emerging Technologies (TRL 1-3):
    - Reviewed 18+ non-conventional HVAC&R technologies
    - Scalability issues (e.g., caloric-based HVAC systems)
  - Potential of Electrochemical Heat Pumps
    - Emphasis on Chemical Looping Heat Pumps
    - 20 – 30 % Energy Saving Reported in ELHP (Cooling Mode)
    - Scalability by Combining with Existing Fuel Cell and Vapor Compression Technologies
    - Ongoing developments in the fuel cell industry and electrochemistry (including selective membranes)

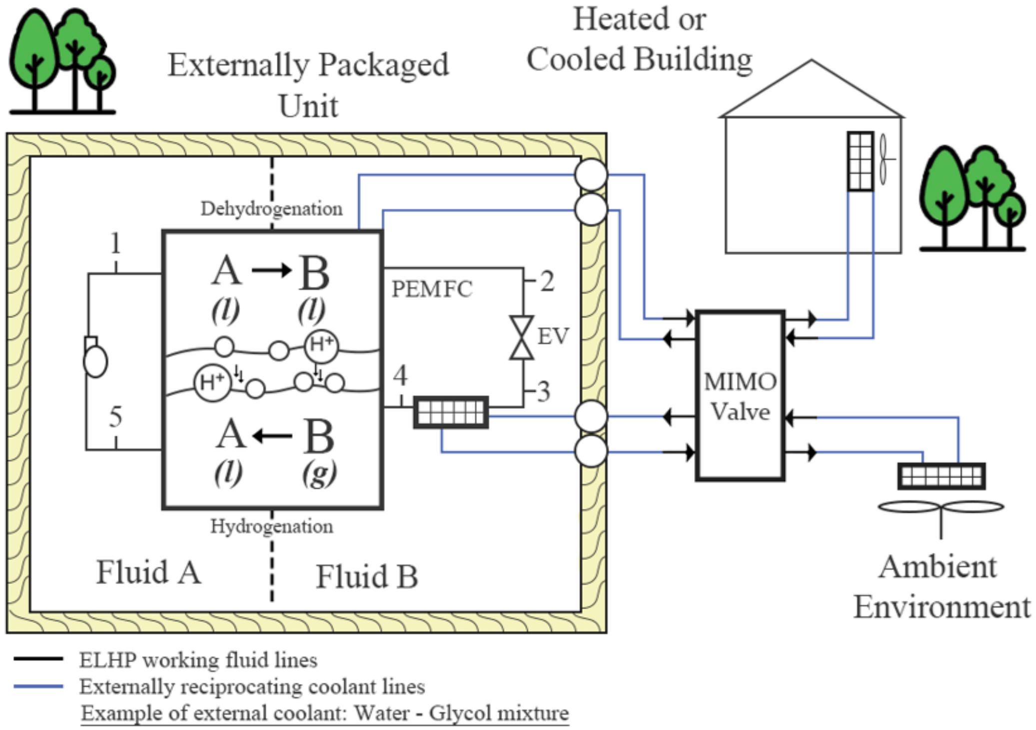




Alignment and Impact (cont'd)

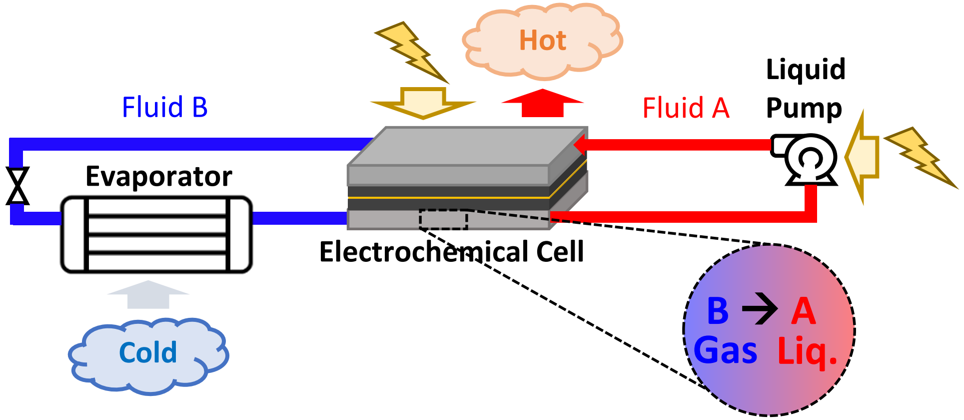
- IMPACT:
  - Novel electrochemistry with ad-hoc thermodynamic "trajectories" to go beyond conventional thermodynamic cycles
  - Natural refrigerant-based heat pump systems (e.g., packaged systems with hydronics)
  - Technoeconomic and scalability of ELHP
  - Future applications: CO2 systems and space habitats

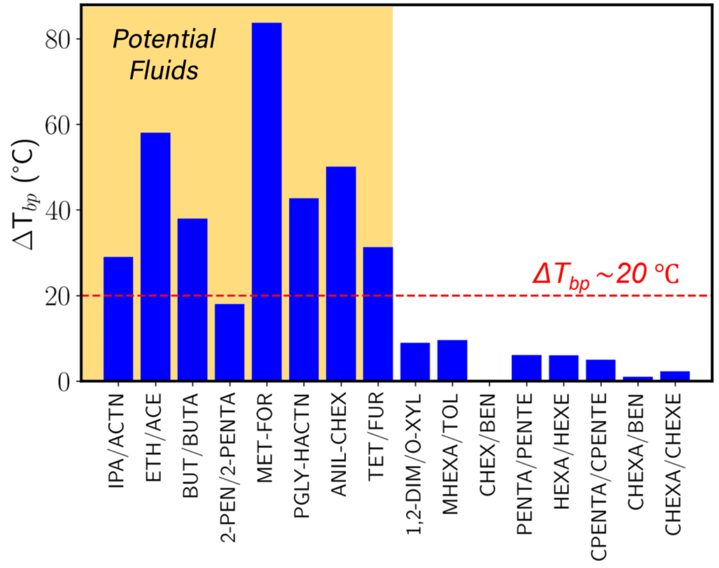




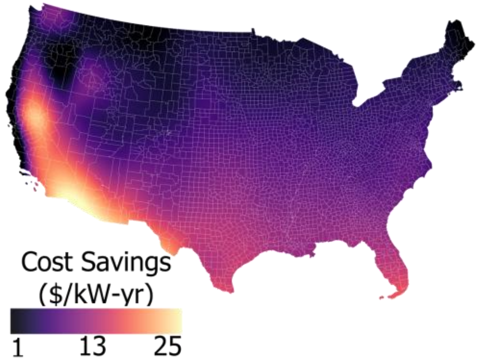
Approach: Overview

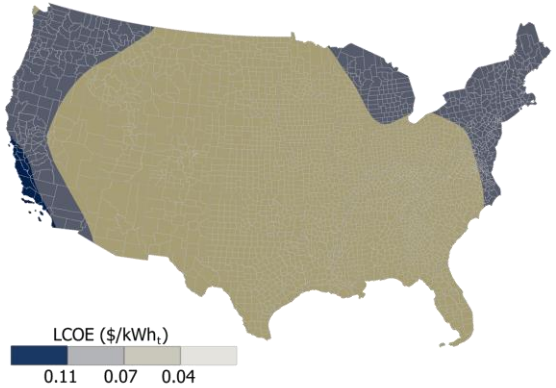
Thermodynamic Assessment and Multi-Scale Modeling



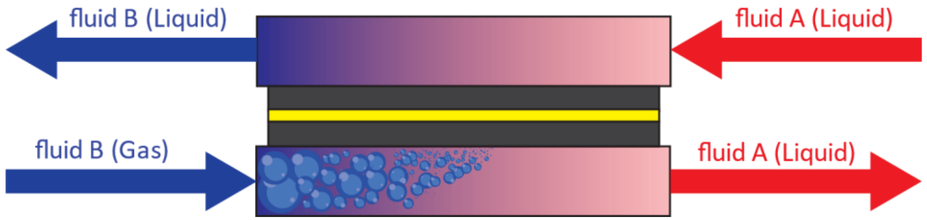


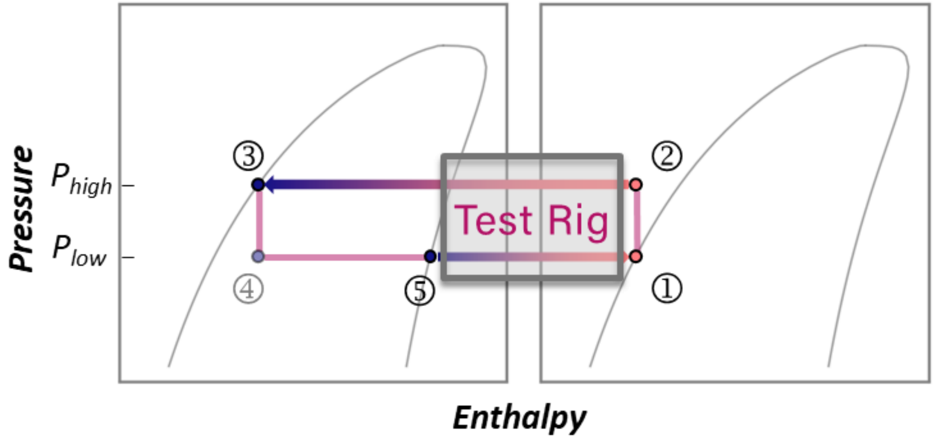
Techno-Economic Analysis





Proof-of-Concept Experiments

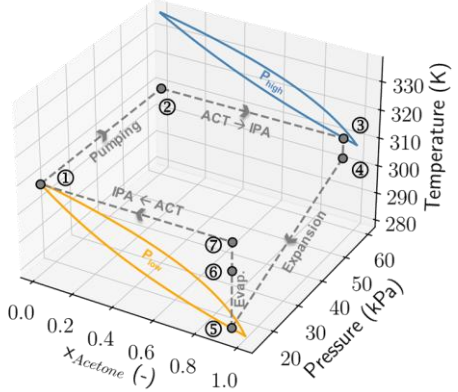


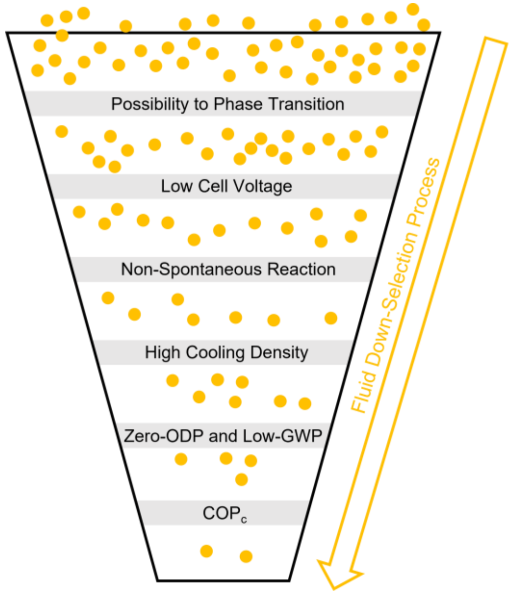


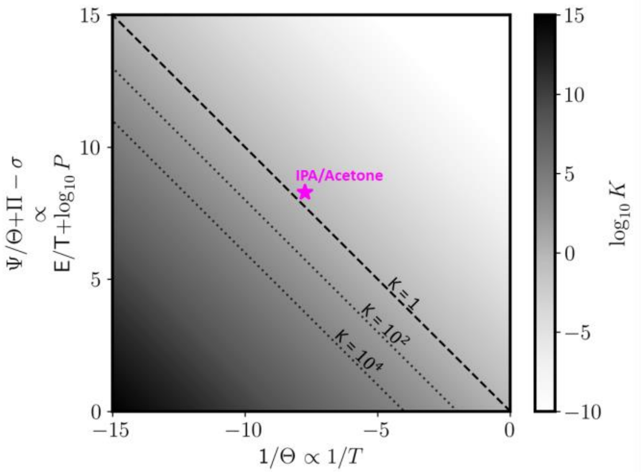
Anode: $(CH_3)CHOH_{(l)} \rightarrow (CH_3)_2CO_{(l)} + 2H^+ + 2e^-$
Cathode: $(CH_3)_2CO_{(g)} + 2H^+ + 2e^- \rightarrow (CH_3)CHOH_{(l)}$
Cell: $(CH_3)_2CO_{(g)} \rightarrow (CH_3)_2CO_{(l)}$

Approach: Overview (Task 2)

- Thermochemical property evaluation (e.g., PC-SAFT), fluid screening, electrochemical potential, stability, cycle assessment, operation in both heating and cooling modes



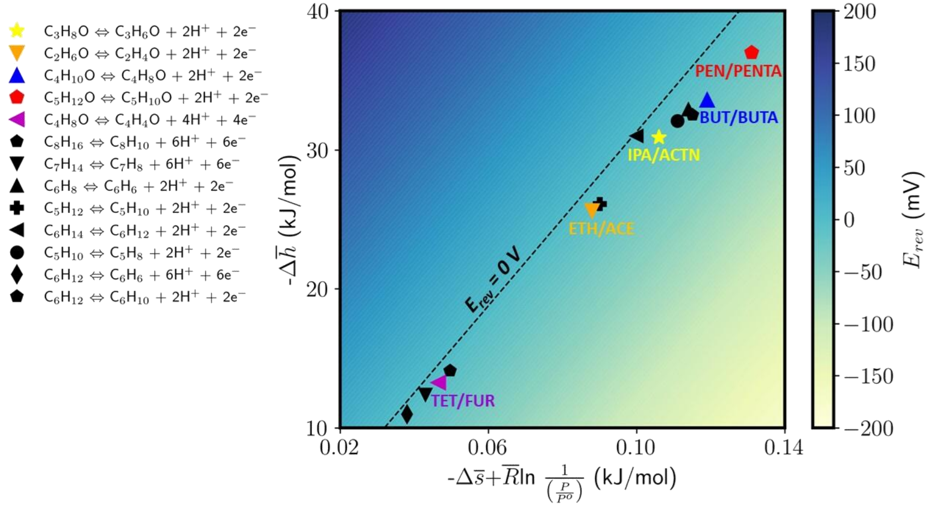


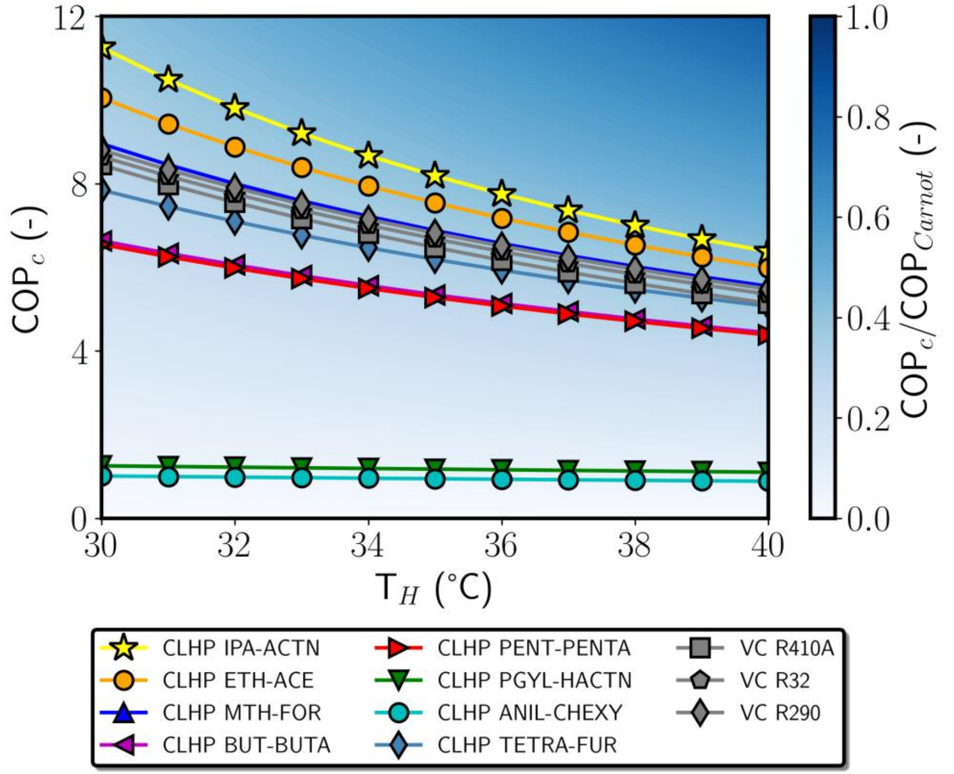


Spontaneous: $K \gg 1$

Equilibrium: $K = 1$

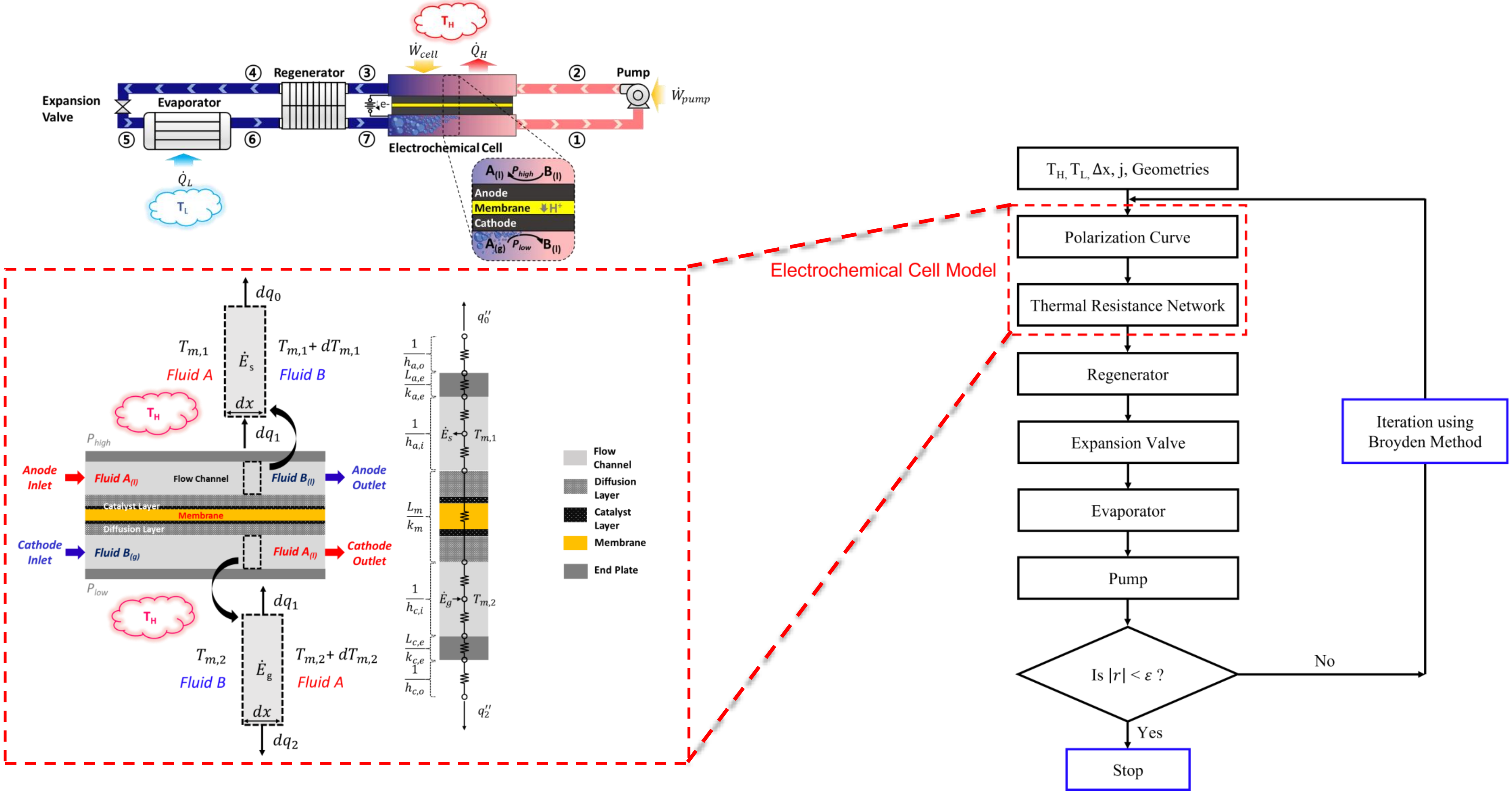
Nonspontaneous: $0 < K < 1$





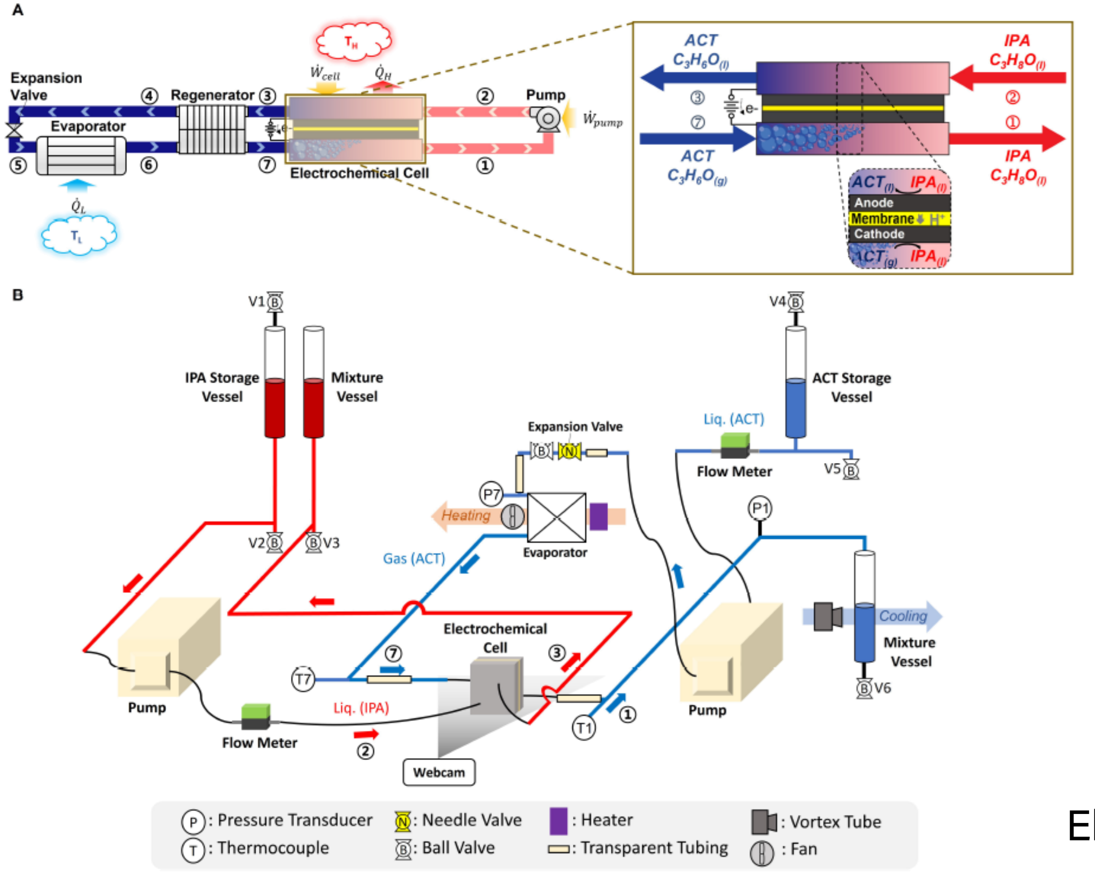
Approach: Overview (Tasks 2, 4)

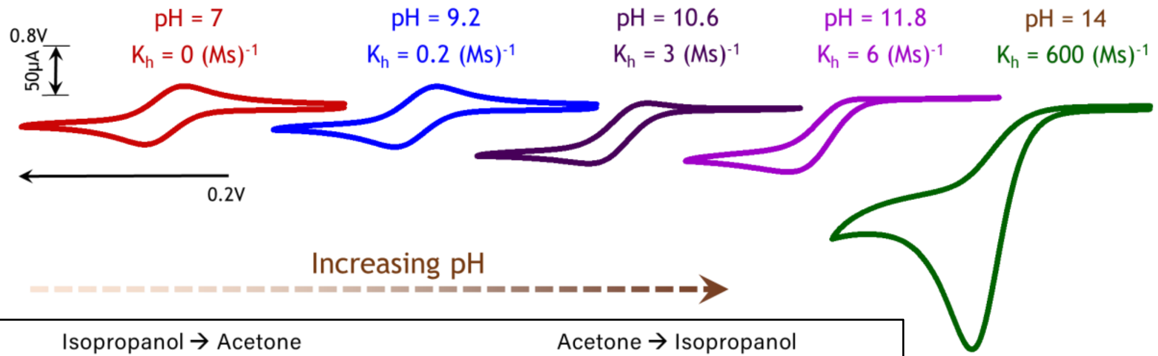
- Detailed cell model and component-based cycle model

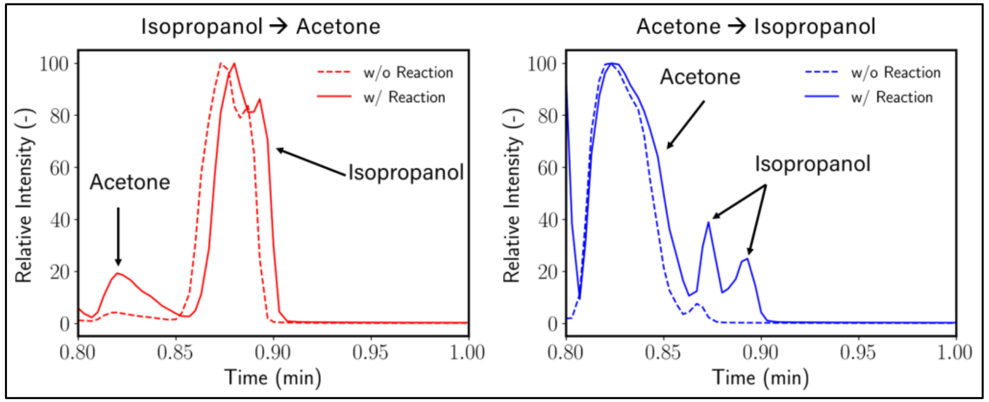


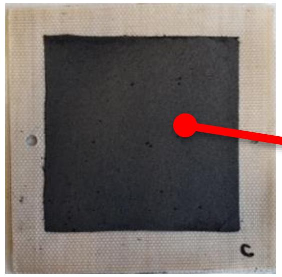
Approach: Overview (Tasks 4, 5)

- **Experimental analyses:**
  - Cell performance characterization for continuous operation
  - Cyclic voltammetry/ Gas Chromatography-Mass Spectrometry (GC-MS) /EDS mapping

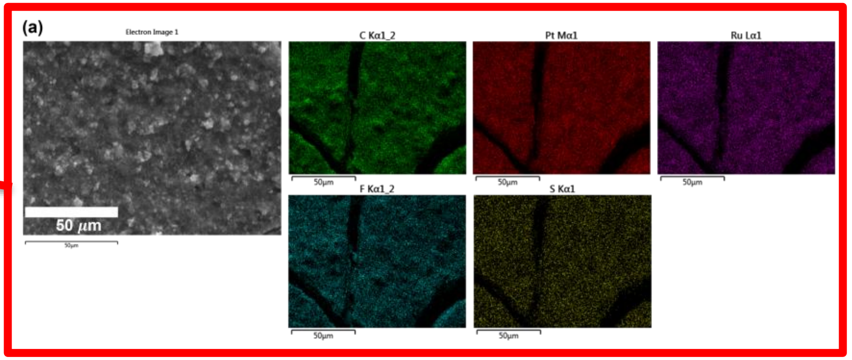








Fabricated Membrane Electrode Assembly (MEA)



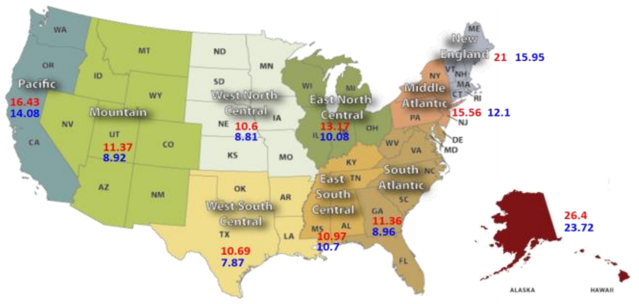
Composition of the surface of the electrode (EDS mapping)

Approach: TEA (Task 3)

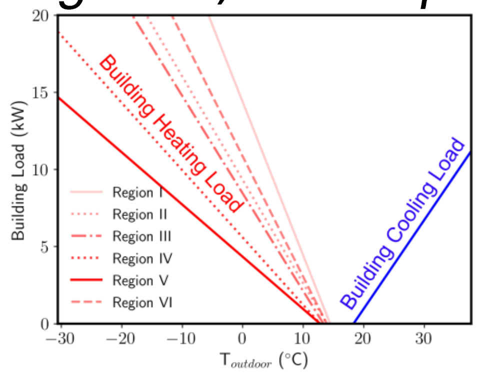
- Operating Costs based on Price of Electricity ($/kWh) and Energy Consumption (kWh/yr)

Operating Costs ($/yr) =

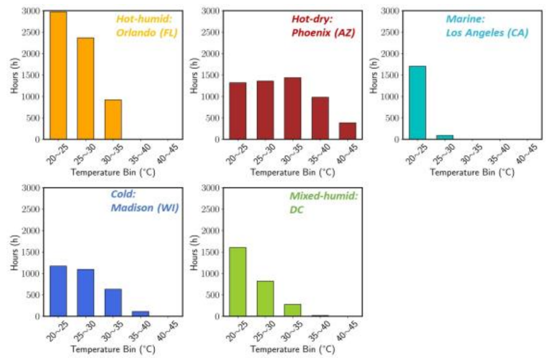
Price of Electricity

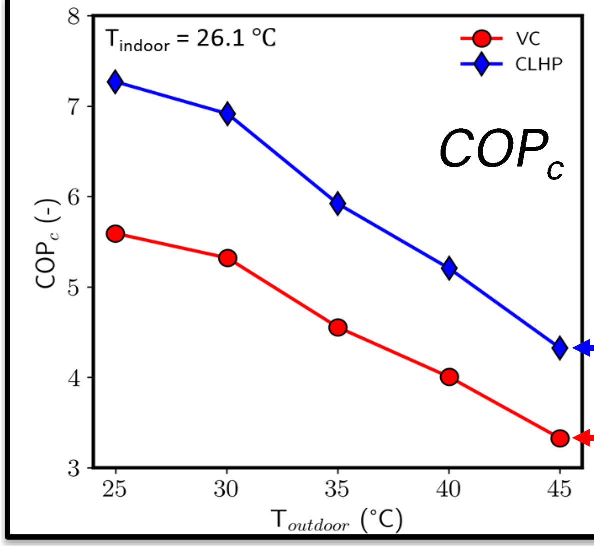


Building Load, Unit Capacity



Bin Weather Data





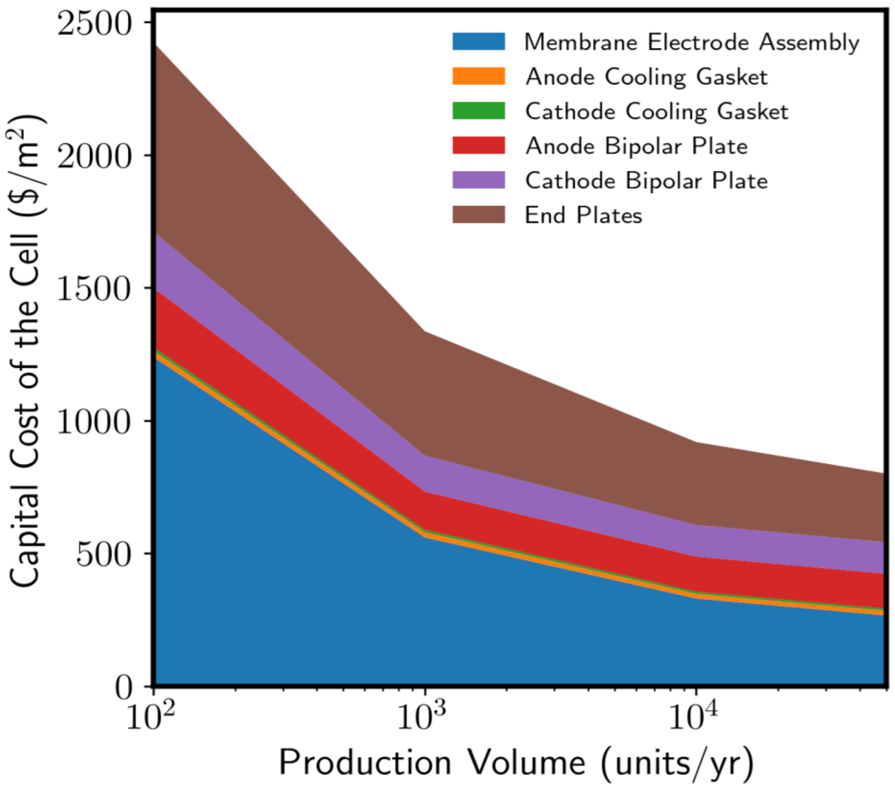
30% COP_c improvements

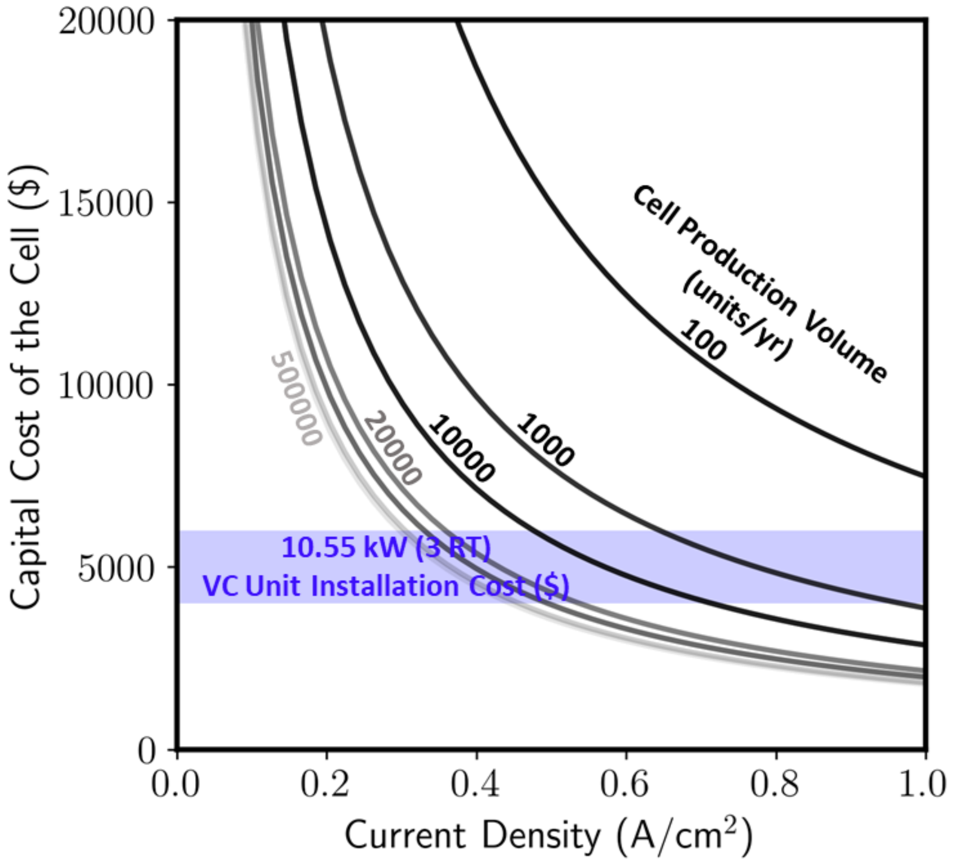
VC data from Cheng et al. (2021) - 10.55 kW (3 RT)

Cheng et al. (2021)

Approach: TEA (Task 3)

- Capital costs data obtained from fuel cell industry as initial analysis
- Coupled costs data and system model
- Economic viability:
  - Production Volume (>2,000)
  - Current Density (>0.4 A/cm2)





Resource: Battelle Memorial Institute (2016)

Approach: Challenges and Risks

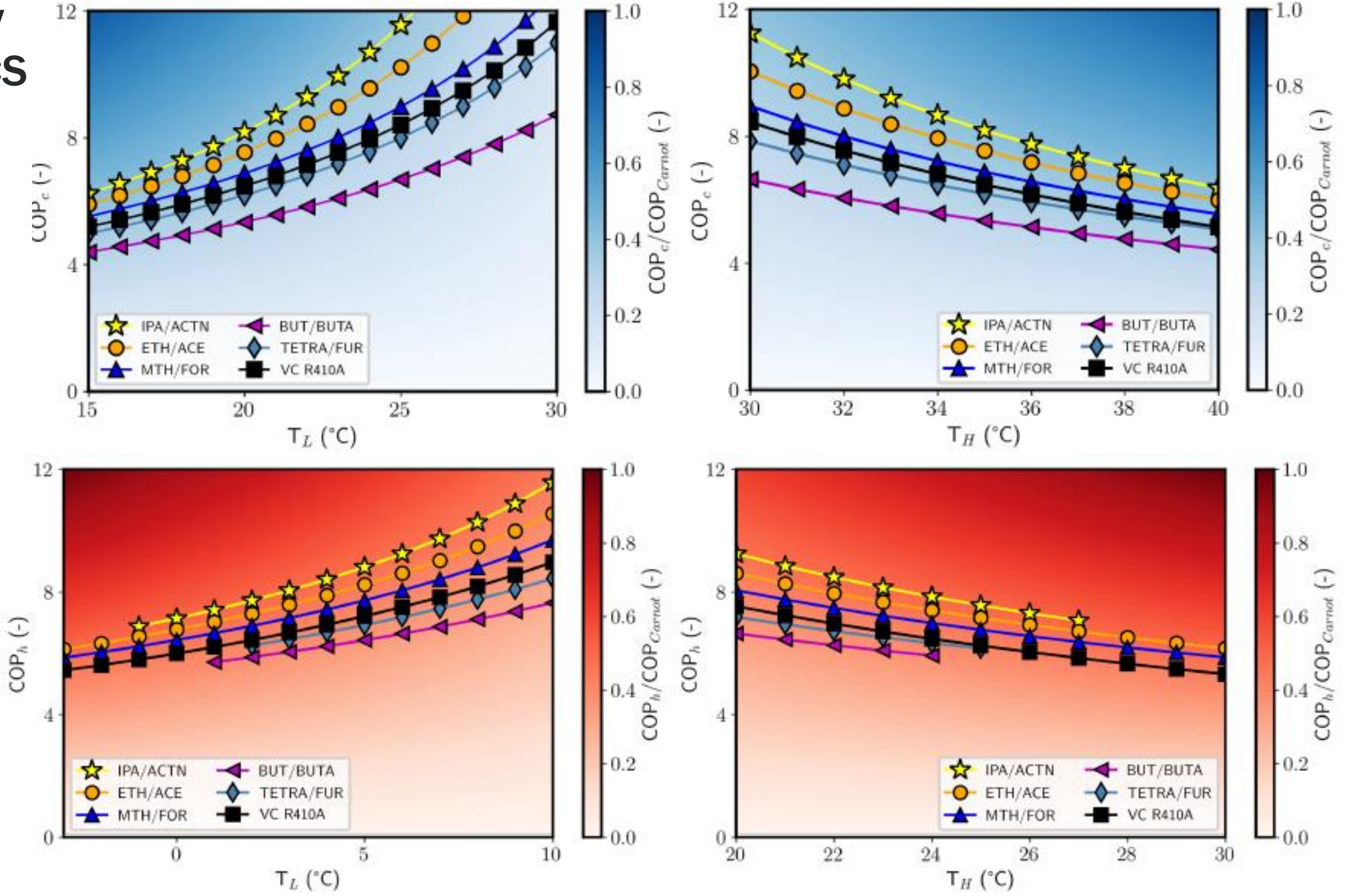
- **Utilizing Purdue's expertise in advanced HVAC&R, UIUC's expertise in electrochemistry, and Carrier's industrial experience to overcome challenges**

#	Challenge	Solution
1	Working Fluid/Material Selections/Electrochemistry	**Purdue:** - Evaluate working fluids using thermodynamic and electrochemical models **UIUC:** - Use exp. characterizations to assess fluid kinetics and reversibility
2	Designing High Performance Cell with Selective Membranes	**Purdue:** - Use ELHP cell test rig to assess the performance - Develop a mechanistic ELHP cell model **UIUC:** - Design, synthesis, and testing of membranes, catalysts, molecules for the electrochemical cell
3	Continuous Operation of ELHP system	**Purdue & UIUC:** - Characterization of reaction completion and cell degradation (e.g., GS-MS) - Collaborate with **Carrier Corp.** for system integration

Progress

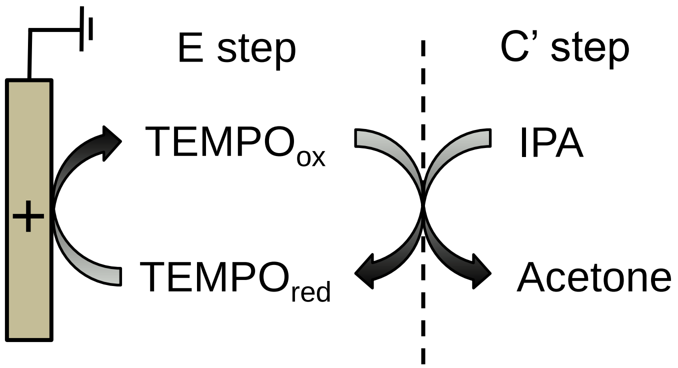
- Potential system efficiency improvements ELHP vs. VCS

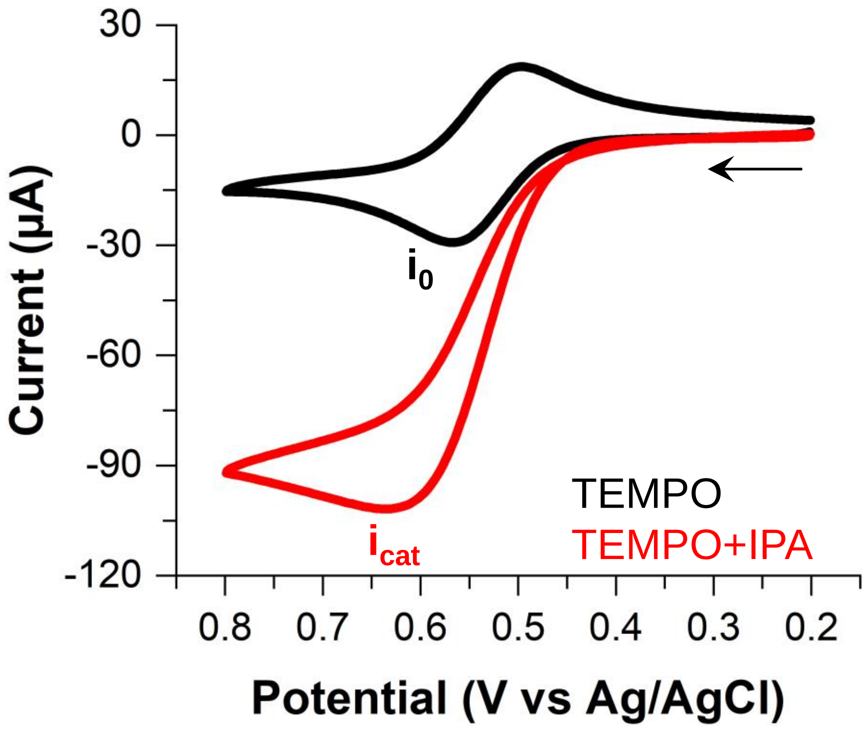
<u>Note on plots:</u> baseline operating parameters are T_H of 35 °C and T_L of 20 °C for cooling mode (upper plots) and T_H of 21.1 °C and T_L of 5 °C for heating mode (lower plots). Pinch point temperature difference is 5 °C for both heat exchangers and electrochemical cell.

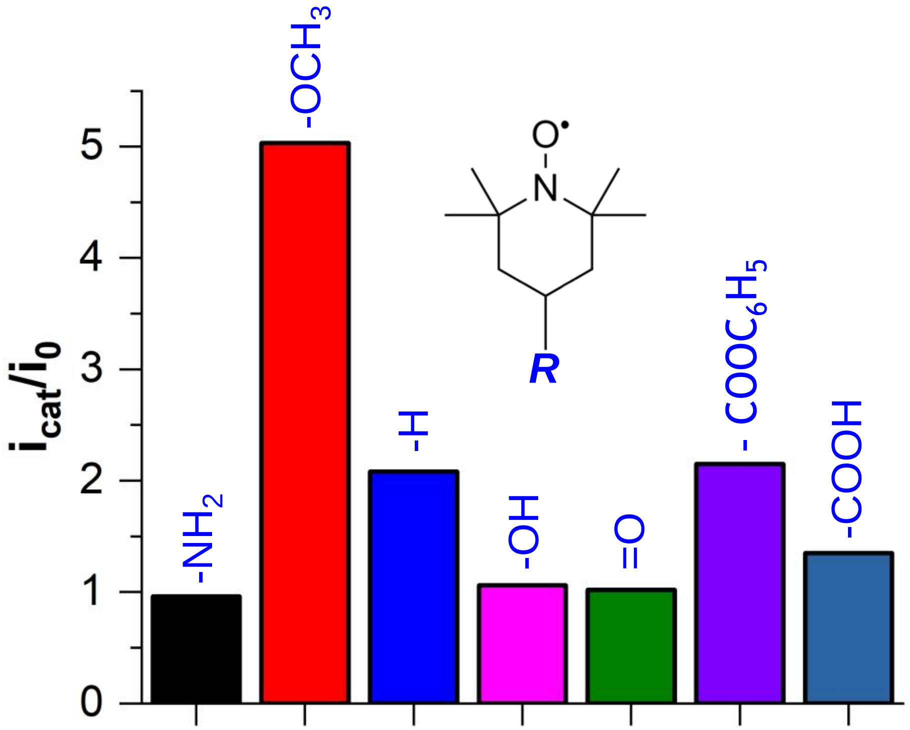


Progress: Catalyst Screening

TEMPO derivatives as molecular electrocatalyst for converting IPA to Acetone







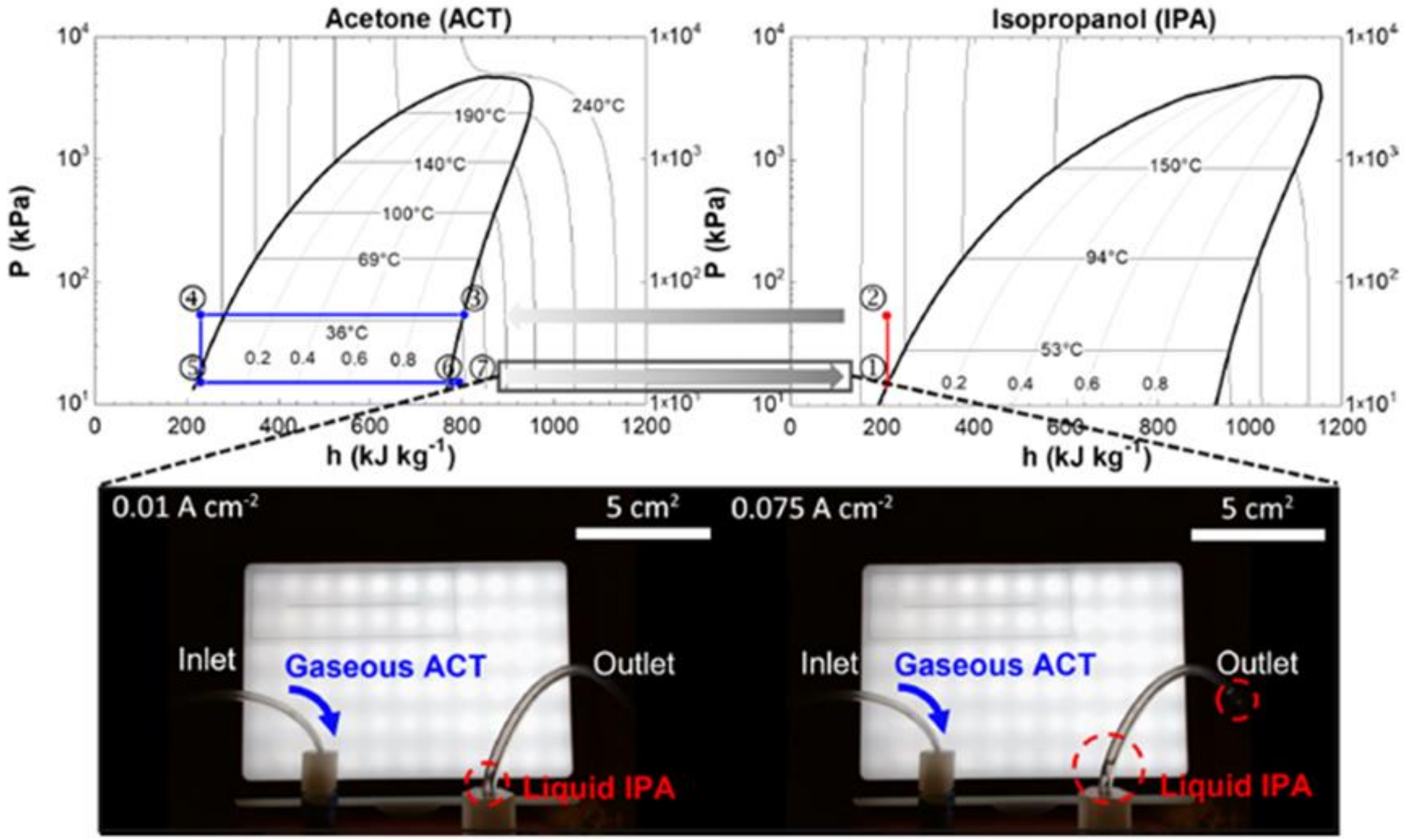
Cyclic voltammetry helped in qualitative screening of molecular catalysts

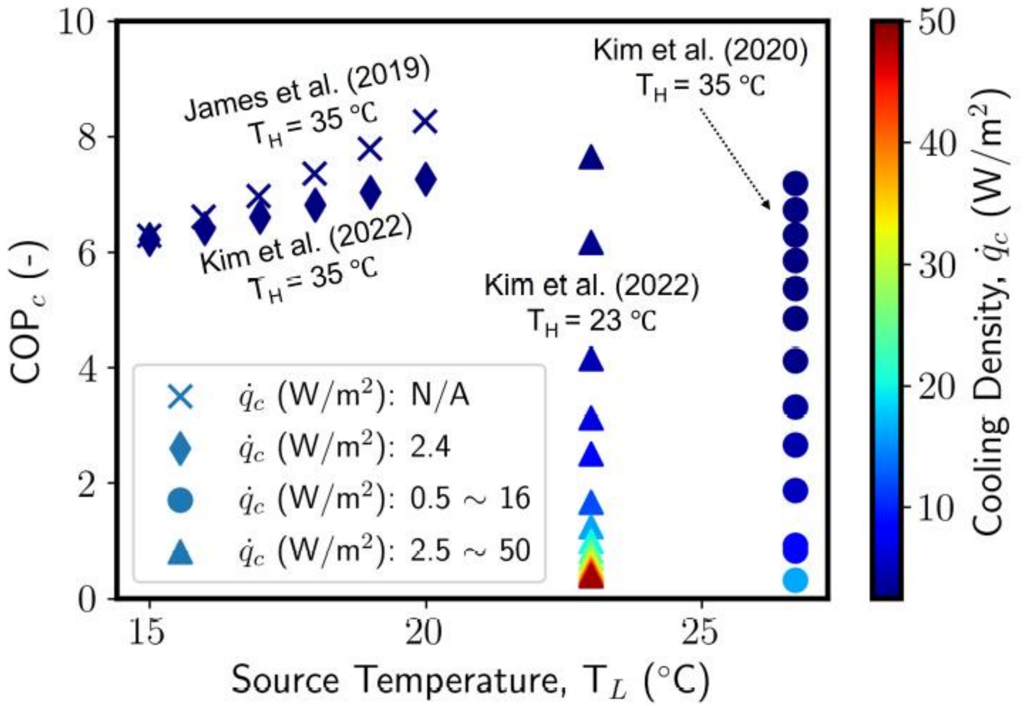
TEMPO and TEMPO-OCH_3 emerged as the most promising candidates

Mishra et al. (2023) DOI: https://doi.org/10.1021/acssuschemeng.2c07419

Progress: Electrochemical Phase Transformation

- Demonstrated the key process enabling ELHP (FY23Q1)



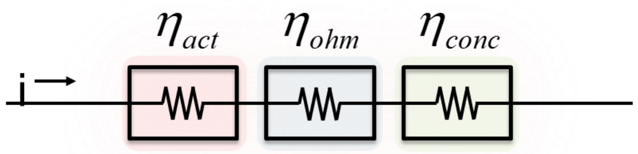


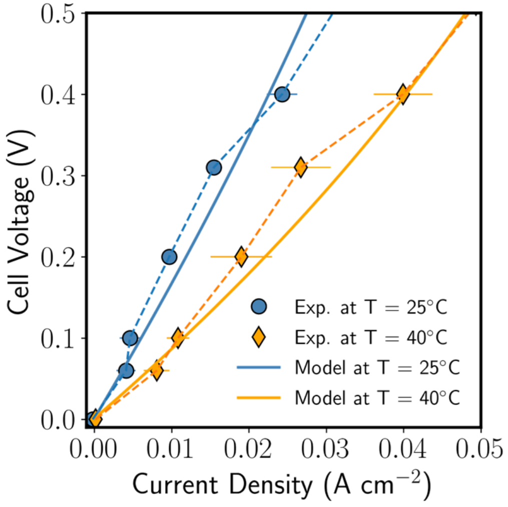
Progress: Overpotential Analysis

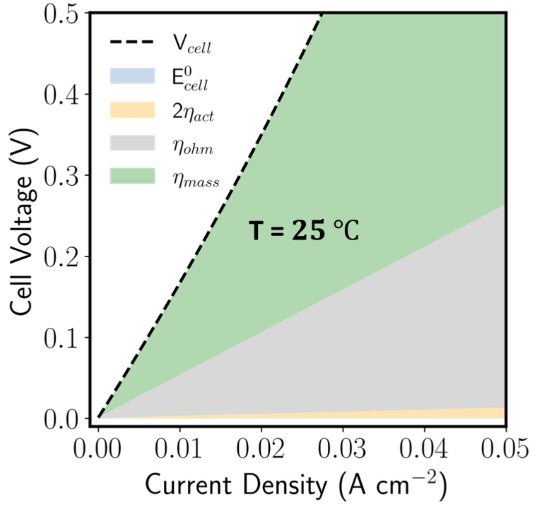
- **Electrochemical model:**

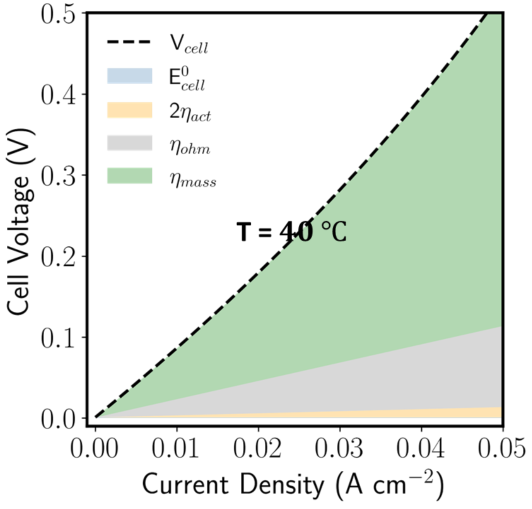
  $V_{cell} = E^0_{cell} + 2\eta_{act} + \eta_{ohm} + \eta_{mass}$

- Breakdown voltage analysis. Ohmic and mass transfer losses account for 90% of losses:
  - Increase in T_{cell}
  - Membrane ($\sigma_{mem} \geq 100$ mS/cm, $L_{mem} \leq 25\ \mu m$)
  - Efficient flow channel and flow rate
  - Catalysts
- Semi-empirical model of losses included in the discretized cell model

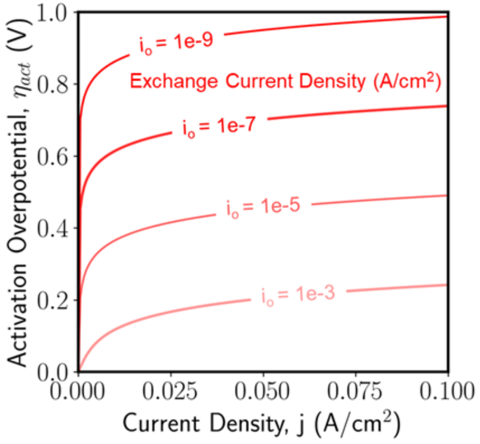




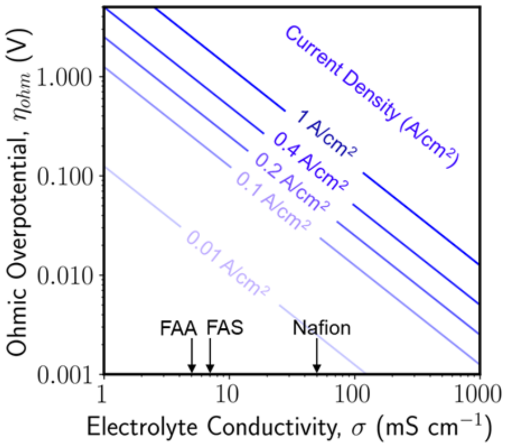




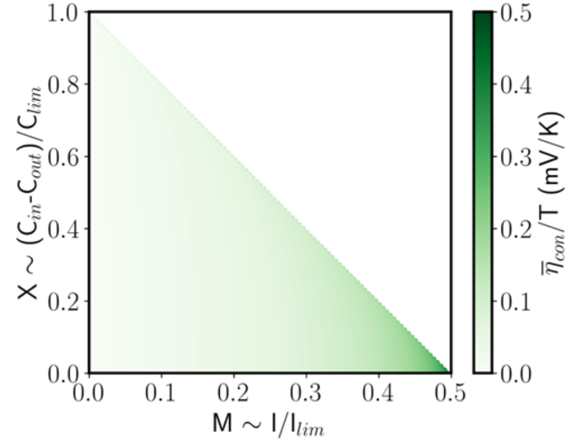
Mapping based on Butler-Volmer equation



Mapping based on Ohm's Law



Mapping based on Nernst equation



Future Work

FY23Q1

1: Program Management

1.2: Finalize Q12 SMART Milestone(s) based on TEA modeling of ELHP systems. The quantitative metrics shall be based on the results obtained during Year II

- Updated SOPO

FY23Q2

2: Advanced ELHP System Designs

2.3: Provide quantitative list of key membrane requirements for down-selected ELHP-system options

FY23Q3

2: Advanced System Models

2.4: Complete gap assessment of best demonstrated performance and commercially viable ELHP system

FY23Q4
FY24Q1
End-Project Goal

3: Advanced System Models

3.3: Update competitive landscape survey and value chain map

3.4: T2M Draft Plan & OTC

4: New ELHP EWFs

4.4: Complete 3-stagescreening

5: High Performance Cells

5.3: Demonstrate > 0.2 A/cm^2 at voltage efficiency $\geq$ 60 % with at least one EWF/ESM

Status of Milestone completion (BP3):

- *Completed*
- *Ongoing:*
  - *Cell efficiency >60% with appropriate catalysts*
  - *Continuous cycle operation*
  - *End of project goal : 0.2 A/cm^2 @ 60% cell efficiency*

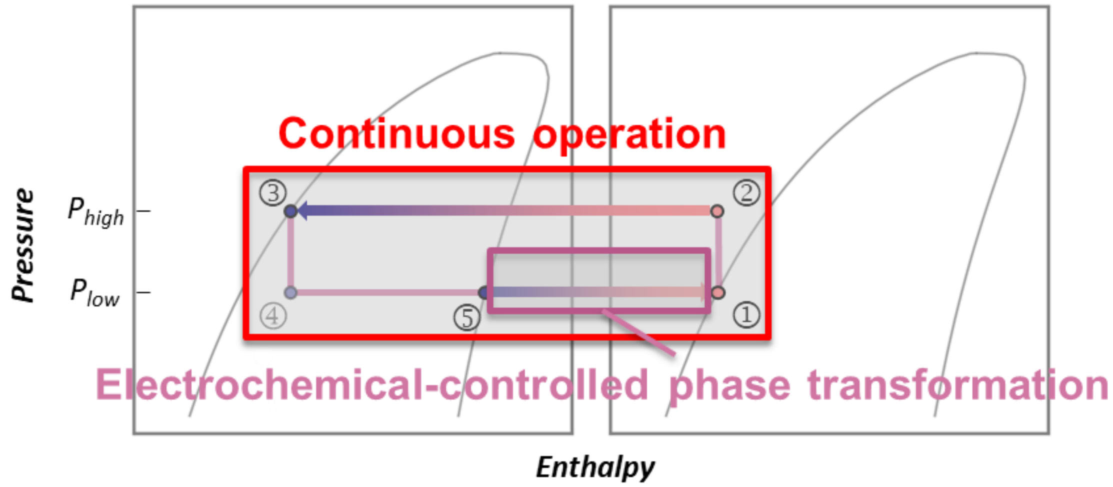
Project Continuation:

- 2023 ASHRAE New Investigator Award (PI Ziviani)

Future Work

- **Advanced System Model (Milestone 2.3 and 2.4, FY23Q2 and Q3):**
  - The determination of the component sizing/design for a given application.
  - Assessment of system performance of a closed loop cycle and economic feasibility.

- **High Performance Cells (Milestone 5.2 and 5.3, FY23):**
  - Optimize electrochemistry of reduction reaction for continuous operation
    - NMR spectra, UV-vis spectroscopy, etc.
  - Demonstrating > 0.1 A/cm^2 (end of project > 0.2 A/cm^2) at voltage efficiency ≥ 60% with at least one EWF.



Thank You

Ray W. Herrick Laboratories, Purdue University; University of Illinois Urbana-Champaign (UIUC); Carrier Corporation
Lead PI: Davide Ziviani, Assistant Professor of Mechanical Engineering, Associate Director of CHPB
PI email: dziviani@purdue.edu
Award Number: DE-EE0008673

REFERENCE SLIDES

Project Execution

	FY2021				FY2022				FY2023			
Planned budget	399,860.00				428,929.00				454,618.00			
Spent budget	216,982.00				227,875.00				30,051.78			
	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
Past Work												
FY22 Q1 M3.2: Market discovery												
FY22 Q1: M2.2 down-selection of ELHP configuration												
FY22 Q1: M4.1 list of fluids												
FY22 Q2: M4.2 Identify one candidate EWF												
FY22 Q2: M5.1 Testing EWF with new cell												
FY22 Q3: M4.3 Update alternative EWF/ESM from M5.1												
FY22 Q4: M5.2 Go/No-Go												
Current/Future Work												
FY23 Q1: Program Management (Update SMART)												
FY23Q2: M2.3 Quantiative list of key membrane requirements												
FY23Q3: M2.4 Complete gap assessment of ELHP												

- **Budget Periods have been shifted due to invoicing delays; underspending is caused by No-Cost Extensions and Work-at-Risk**
- [Go/No-Go 1: Completed] Down-selected ELHP: COP improvement of >20% over VC cycles and the projected capital cost of this system enables a simple payback of ≤ 3 years
- [Go/No-Go 2] Down-selected ELHP: COP improvement of >20% over VC cycles and the projected capital cost of this system enables a simple payback of ≤ 3 years

Team

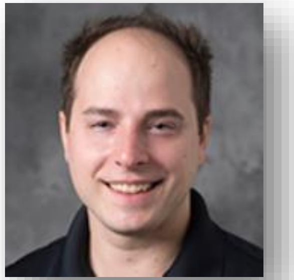
Junyoung Kim
Ph.D. in Mechanical Engineering, Purdue Univ. (Graduated)

Mingjie Zhu
Ph.D. Student in Mechanical Engineering, Purdue Univ.

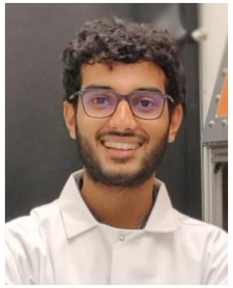
Jinwoo Oh
Postdoctoral Researcher in Mechanical Engineering, Purdue Univ.

James E. Braun, Ph.D.
Herrick Professor of Engineering, and Director of the Center for High Performance Buildings, Purdue Univ.

Eckhard A. Groll, Ph.D.
William E. and Florence E. Perry Head of Mechanical Engineering, and Reilly Professor of Mechanical Engineering, Purdue Univ.



Davide Ziviani, Ph.D.
Assistant Professor of Mechanical Engineering, and Associate Director of the Center for High Performance Buildings, Purdue Univ.



Abhiroop Mishra
Ph.D. Student, Univ. of Illinois at Urbana Champaign (Obtained Link Fellowship)

Aravind Baby
Ph.D. Student, Univ. of Illinois at Urbana Champaign

Raghuram Gaddam
Ph.D. Student, Univ. of Illinois at Urbana Champaign

Joaquin Rodríguez-López, Ph.D.
Associate Professor of Chemistry, and a Faculty of Beckham Institute for Advanced Science and Technology, Univ. of Illinois at Urbana Champaign

Members:

- 4 Professors
  - Mechanical Eng. (3)
  - Chemistry (1)
- 3 PhD students and 1 Postdoc.
  - Purdue (2)
  - UIUC (3)

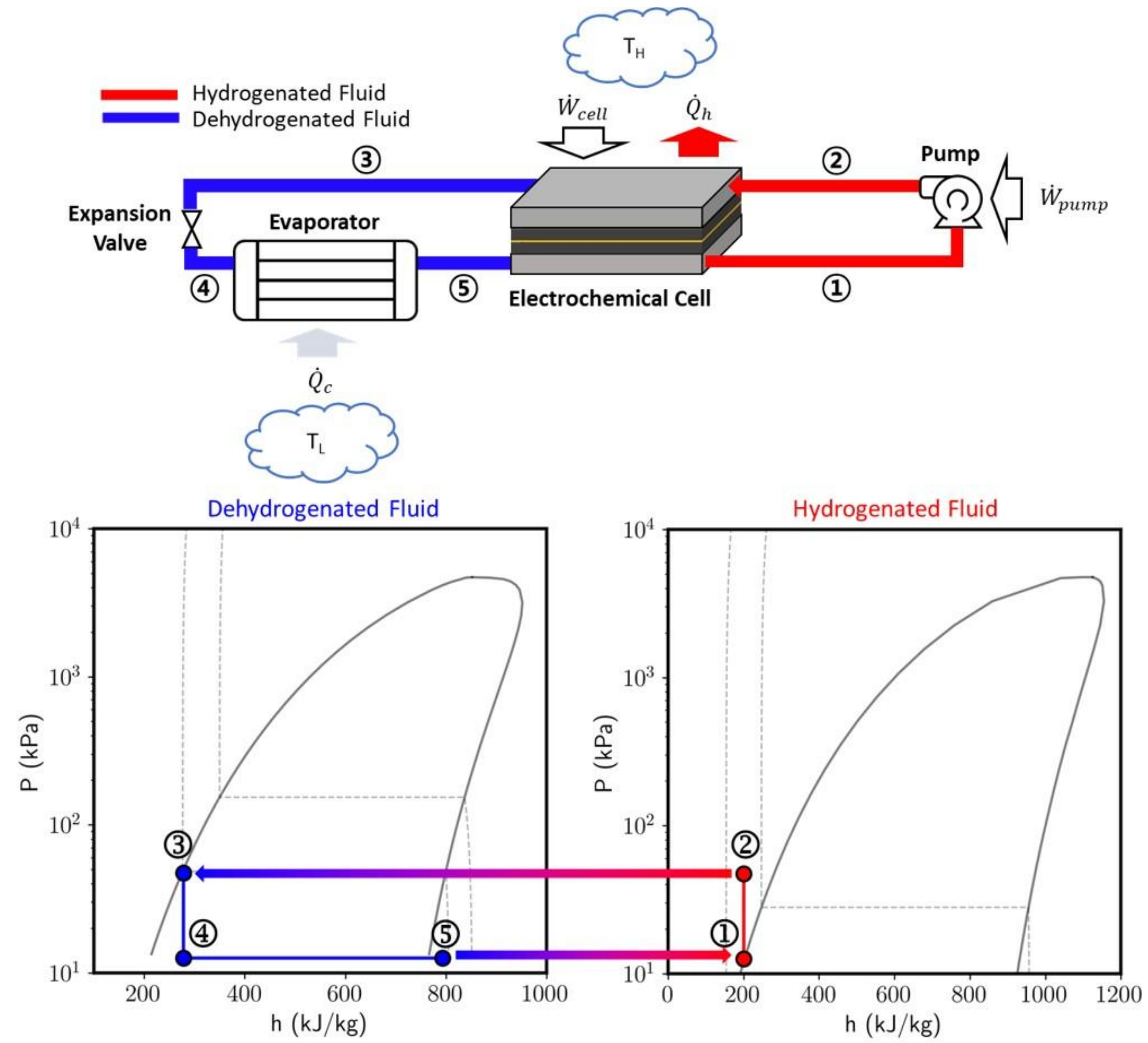
Team

- Purdue and UIUC teams have interacted with **Carrier Corporation**
  - Key contacts: Larry Burns, Allen Chard Kirkwood, Hafez Raeisi Farad

- Discuss a future **scalability** of ELHP system (Y3) with Carrier Corp.

- **Regular research meeting** with Carrier Corporation

Supplementary Information: CLHP Working Principle



- **Working Principle:** Volatility controlled by breaking or reducing a hydrogen bond via electrochemical reaction

Dehydrogenated Fluid (more volatile)

$$A \leftrightarrow AH_2$$

Hydrogenated Fluid (less volatile)

James et al. (2019), Kim et al. (2021)

Supplementary Information: Overpotentials

Overpotentials	Expressions	Nomenclatures
Activation (η_{act})	$\eta_{act} = \frac{RT_{cell}}{0.5n_eF}\sinh^{-1}\left(\frac{j}{2i_0 exp\left(-\frac{E_{act}}{R}\left(\frac{1}{T_{cell}}-\frac{1}{T_{ref}}\right)\right)}\right)$	R: universal gas constant (J/mol-K) T_{cell}: cell temperature (°C) n_e: number of electrons transferred (-) F: Faraday's constant (C/mol) j: current density (A/cm^2) i_0: exchange current density (A/cm^2) E_{act}: activation energy (J/mol) T_{ref}: reference temperature (°C)
Ohmic (η_{ohm})	$\eta_{ohm} = IR_{mem}$ $R_{mem} = \frac{L_{mem}}{\sigma}$	I: current (A) R_{mem}: membrane resistance (Ω) L_{mem}: thickness of the membrane (cm) σ: membrane conductivity (mS/cm)
Mass (η_{mass})	$\eta_{mass} = c\ln\left(\frac{j_{lim}}{j_{lim}-j}\right)$ $j_{lim} = \frac{n_eFDC_0^B}{\delta}$	c: effective value (an empirical constant) (-) j_{lim}: limiting current density (A/cm^2) D: diffusion coefficient (cm^2/s) C_0^B: bulk concentration (mol/cm^3) δ: diffusion layer thickness (cm)

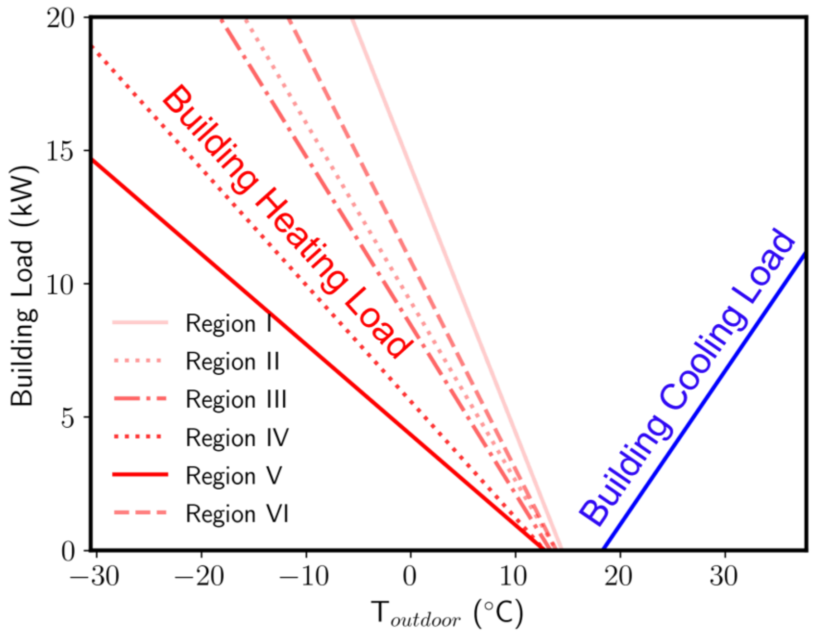
Supplementary Information: LCOE ($/kWh$_t$)

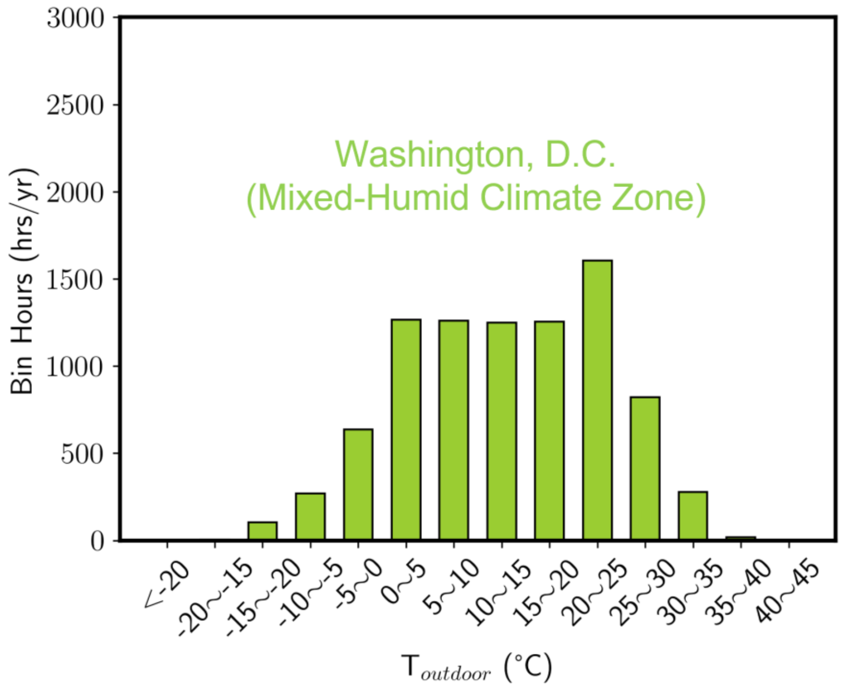
Parameter	Description	Value(s)	Reference
C_{ELHP}	ELHP capital cost per unit rated cooling capacity	500 $/kW$_t$ ~ 1,000 $/kW$_t$	Kim et al. (2022)
C_{VC}	VC capital cost per unit rated cooling capacity	360 $/kW$_t$ ~ 460 $/kW$_t$	U.S. EIA (2018)
COP_{VC}	Average COP_{VC} for both cooling and heating (reference)	Average: 2.9 (-) Heating: 3.3 (-); Cooling: 2.5 (-)	Lee et al. (2021)
COP_{ELHP}/COP_{VC}	Average COP improvement for both in cooling and heating	1.1 ~ 1.3 (-)	James et al. (2019); Kim et al. (2022)
$\dot{Q}$	Unit cooling capacity (heating capacity is in the range of 10.55 kW$_t$)	10.55 kW$_t$	-
Q	Amount of annual cooling and heating delivered	10,000 kWh$_t$/yr ~ 40,000 kWh$_t$/yr	-
LT	Lifetime of the system	10 yrs	-
POE	Price of electricity	0.13 $/kWh$_e$ and 0.23 $/kWh$_e$	U.S. EIA (2021)
r	Discount rate	3%	-

Supplementary Information: LCOE ($/kWh$_t$)

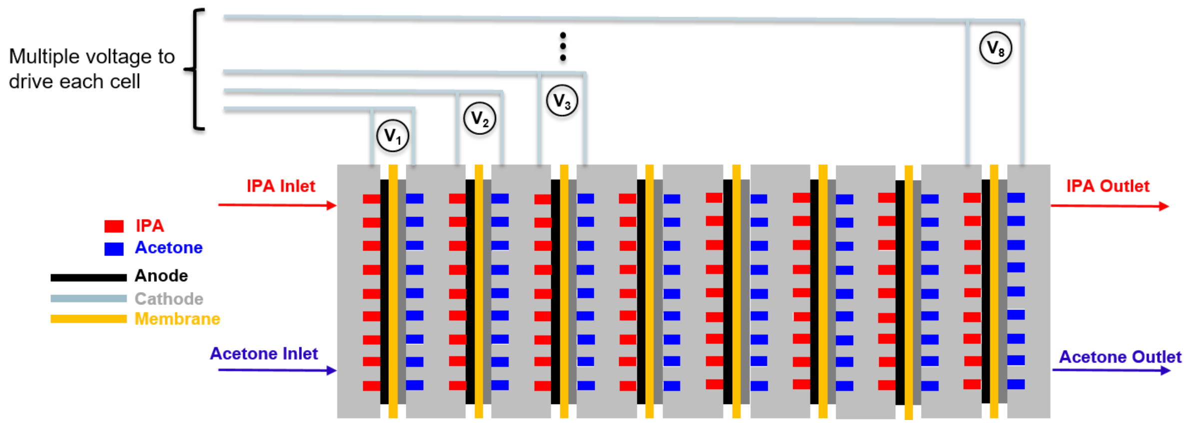
- **Annual cooling and heating delivered:**
  - Bin method
  - Building load profiles adapted from AHRI Standard 210/240 (2023)
  - Bin weather data from the contiguous United States

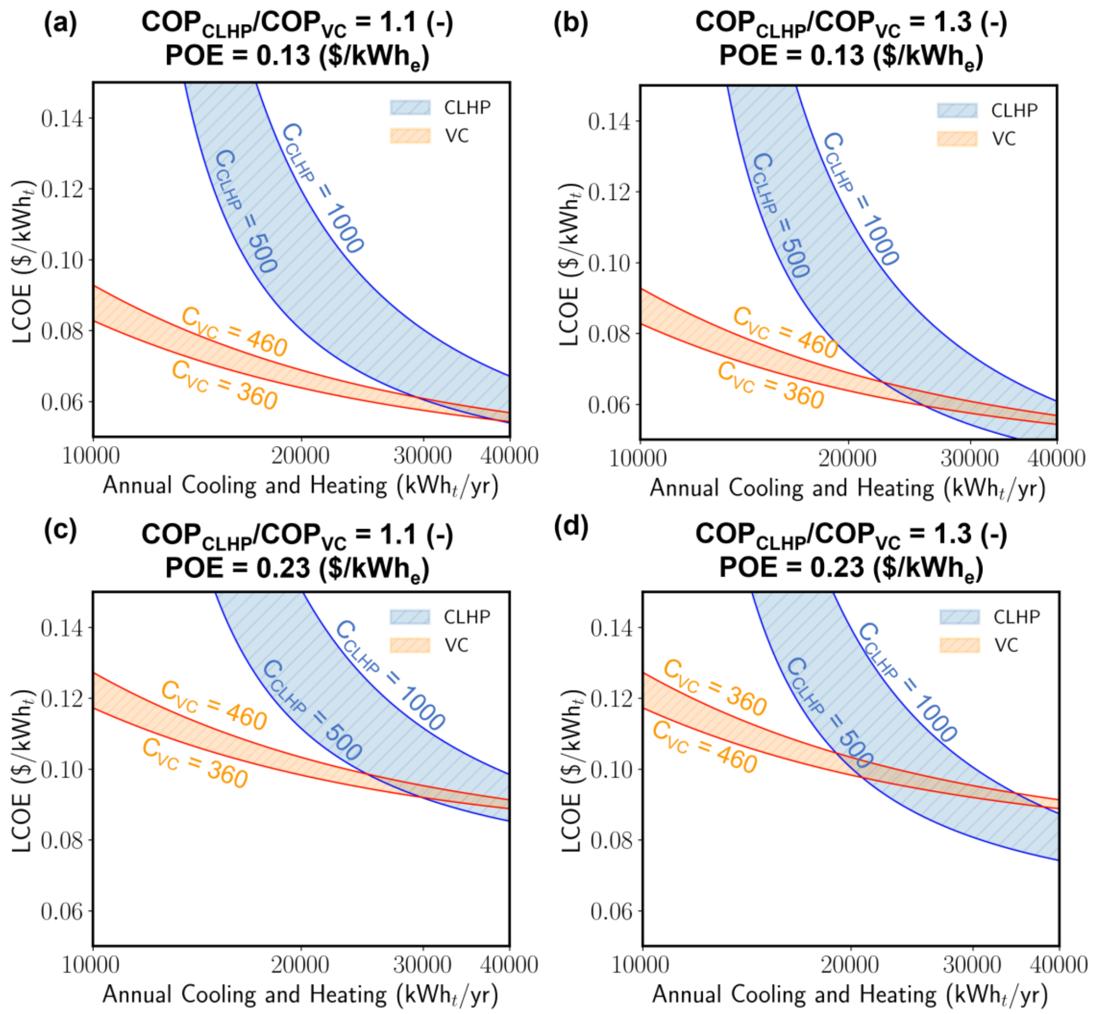
$$LCOE = \frac{C \cdot \dot{Q}}{Q \cdot LT} + \frac{POE}{COP}$$





Supplementary Information: LCOE ($\$/kWh_t$)

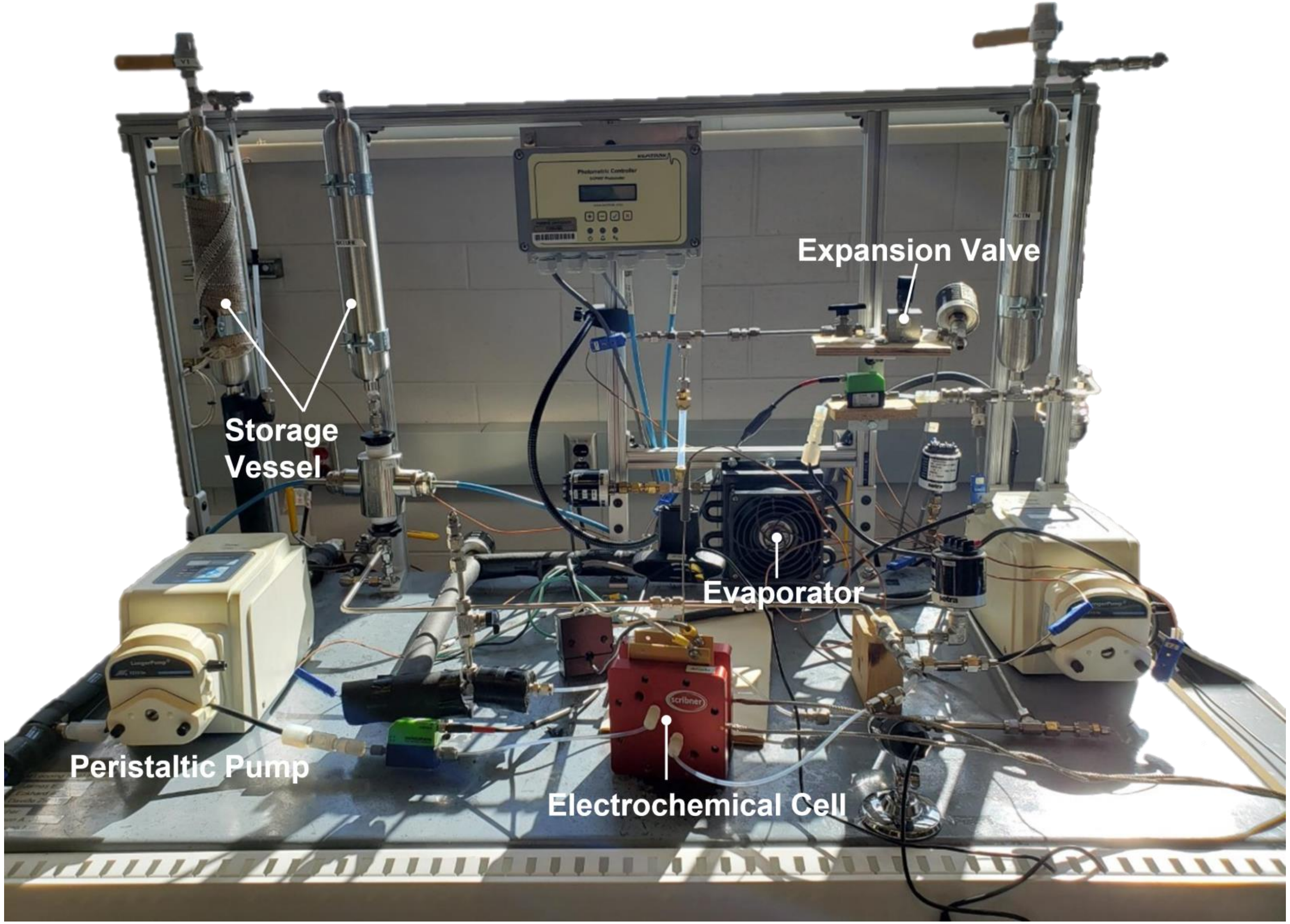




Supplementary Information: Membrane Electrode Assembly

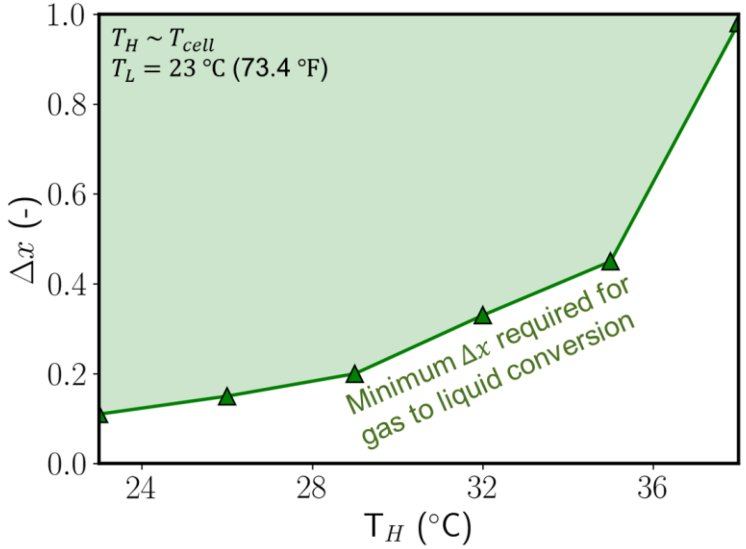
Category	MEA1	MEA2	MEA3	MEA4
Membrane	SPEEK (75 μm)	SPEEK (75 μm)	Nafion XL (25 μm)	Nafion XL (25 μm)
Gas Diffusion Layer for Anode and Cathode	Sigracet 39 BB (125 μm)	Sigracet 39 BB (125 μm)	Sigracet 39 BB (125 μm)	Sigracet 39 BB (125 μm)
Catalyst for Anode	3.5-4.0 mg/cm^2 PtRu/C	3.5-4.0 mg/cm^2 PtRu/C	25 mM TEMPO 0.1M Na_2CO_3 1.5M IPA in H_2O	3.5-4.0 mg/cm^2 PtRu/C
Catalyst for Cathode	3.5-4.0 mg/cm^2 PtRu/C	3.5-4.0 mg/cm^2 Pd/C	3.5-4.0 mg/cm^2 Pd/C	3.5-4.0 mg/cm^2 Pd/C
Gasket	Teflon-Impregnated Fiberglass Gasket (254 μm)	Teflon-Impregnated Fiberglass Gasket (254 μm)	Teflon-Impregnated Fiberglass Gasket (254 μm)	Teflon-Impregnated Fiberglass Gasket (254 μm)

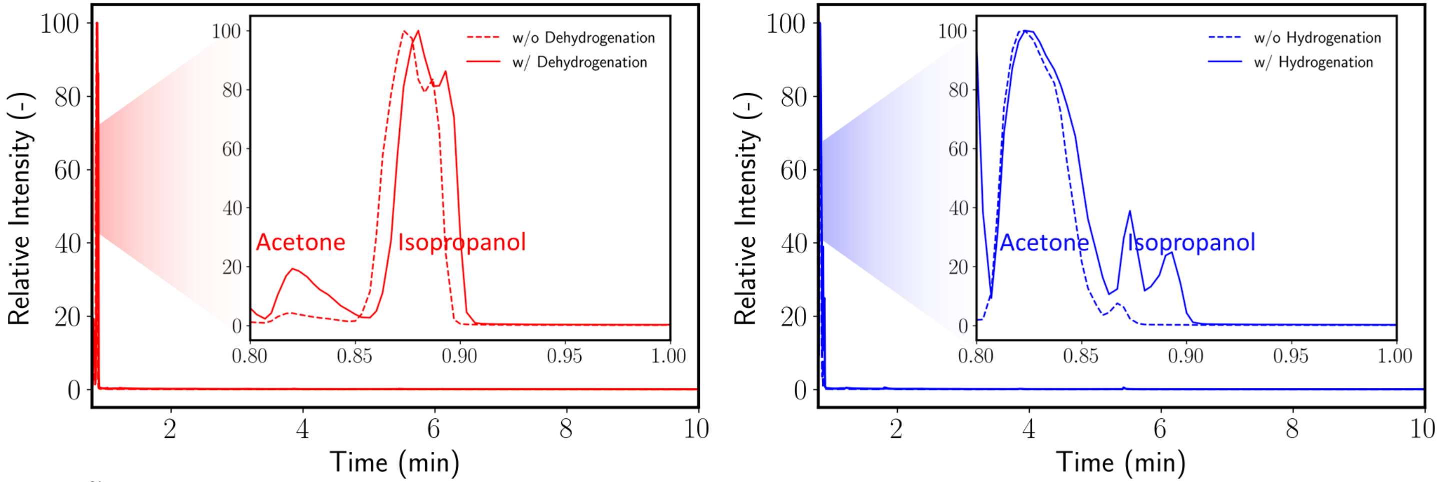
Supplementary Information: Experimental Setup

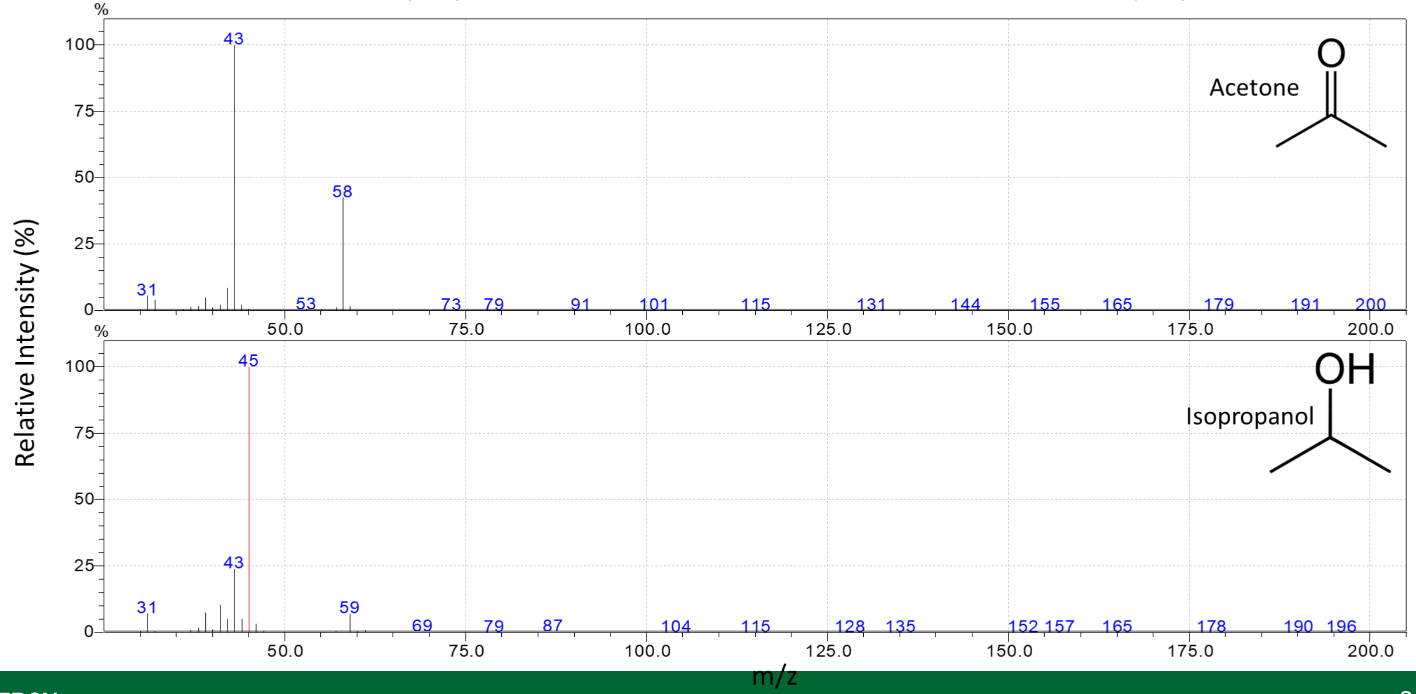


Supplementary Information: Experimental Setup

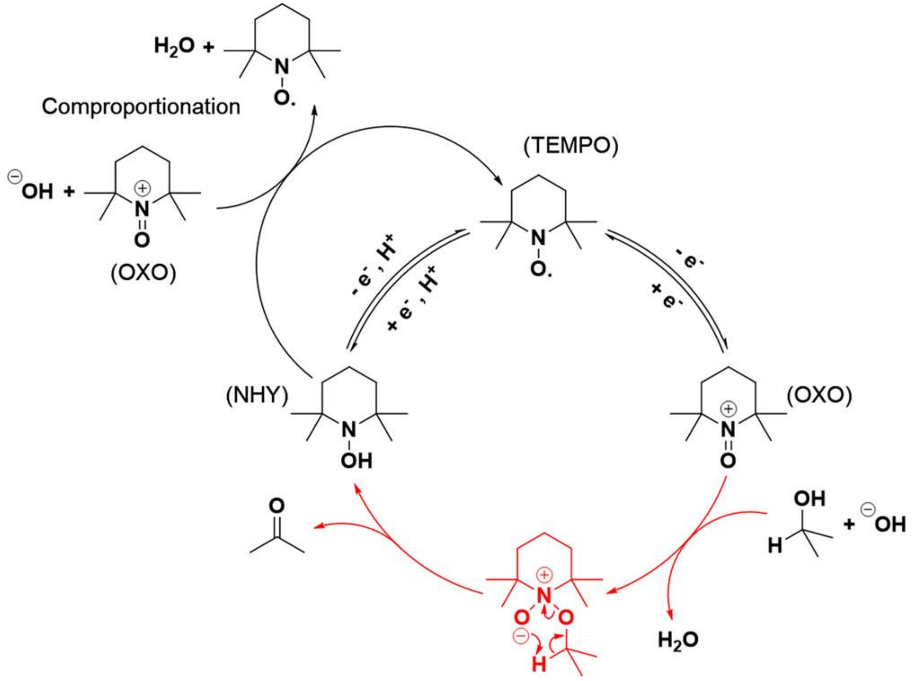
- **Gas Chromatography-Mass Spectrometry (GC-MS):**
  - Detect acetone (0.82 min) and isopropanol (0.87 min)
  - Reaction confirmed by mass spectrum
- **Extent of the reaction:**
  - Increase in cell temperature → Increase in the minimum required Δx.
  - ∵ IPA also could be vaporized.
  - Larger cell area is needed.



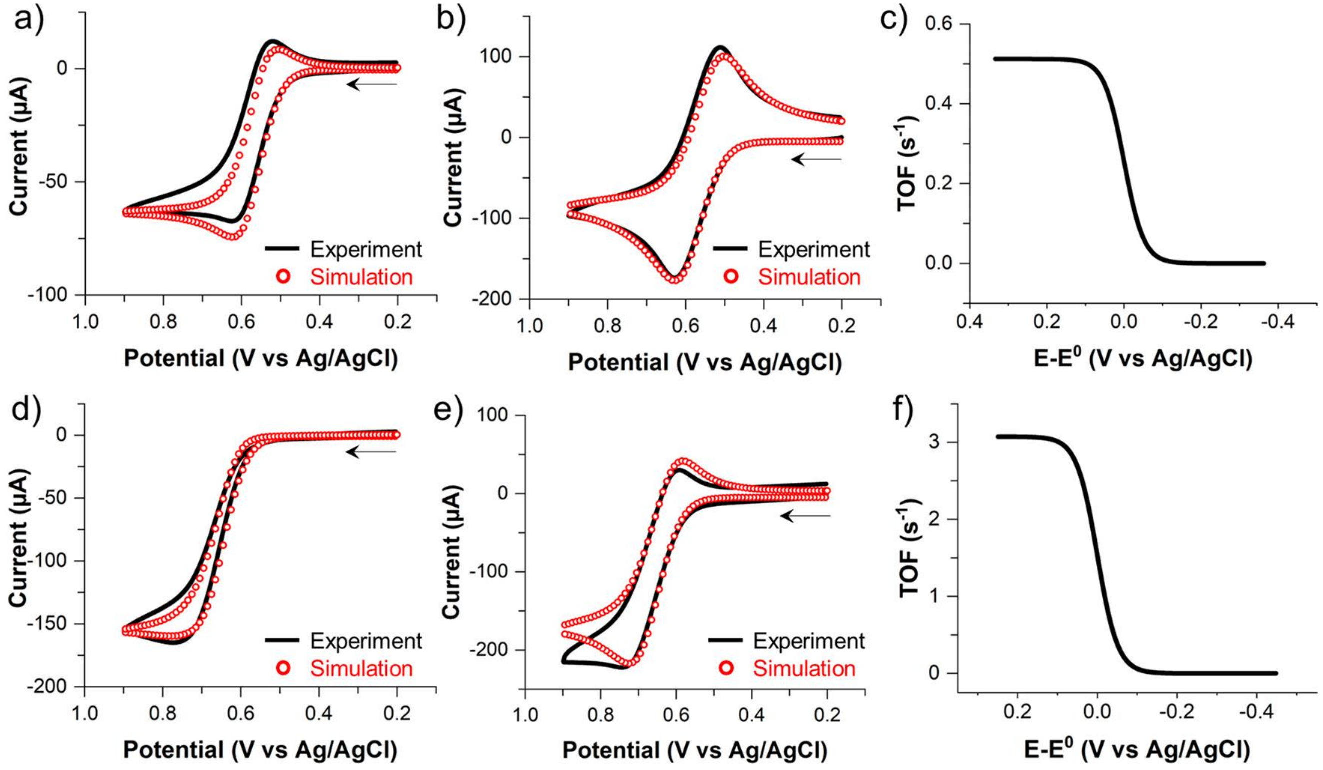




Supplementary Information: TEMPO

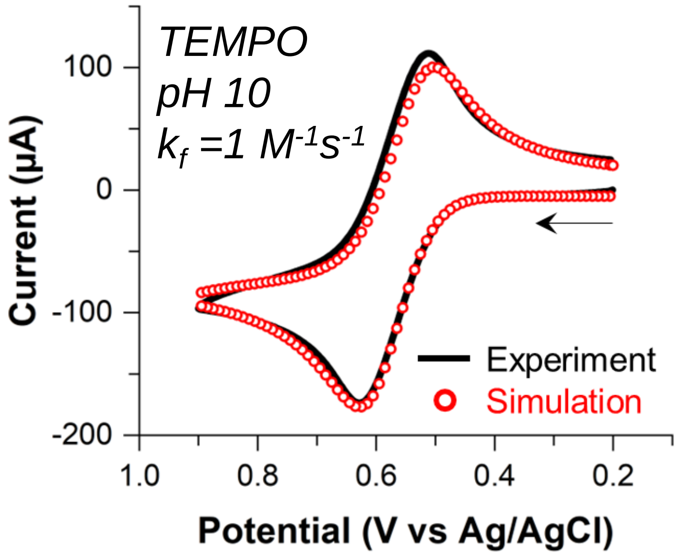


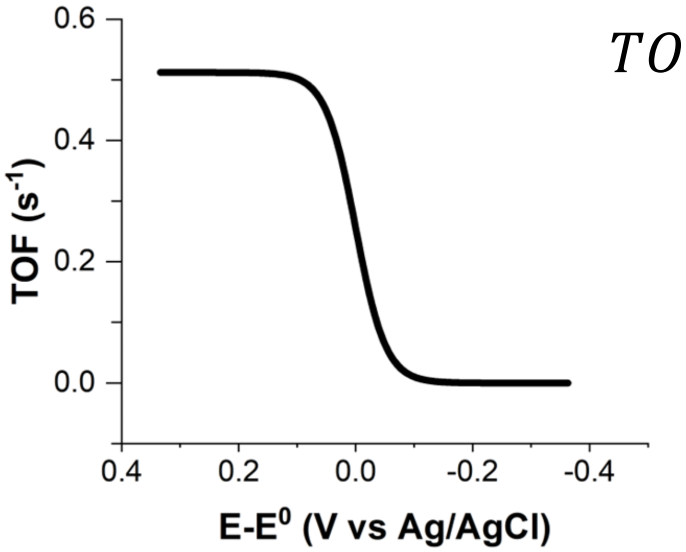
Proposed Mechanism for the TEMPO Mediated IPA Oxidation to Acetone with the Catalytic Step Highlighted in Red Color



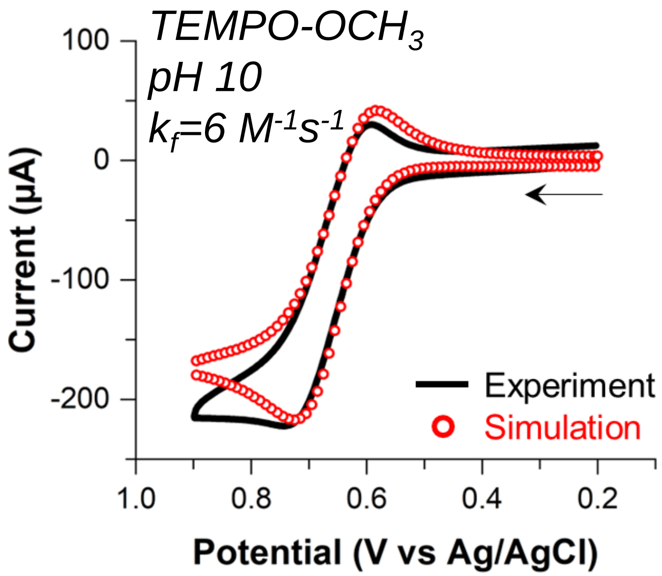
Experimental and simulated voltammograms for the rate constant (k_f) characterization. Experimental and simulated (with k_f as 1 M^{-1} s^{-1}) CVs of 5 mM TEMPO 250 mM IPA aqueous solution (pH 10) at a) 50 mV/s and (b) 500 mV/s scan rate. Experimental and simulated (with k_f as 6 M^{-1} s^{-1}) CVs of 5 mM TEMPO-OCH_3 250 mM IPA aqueous solution (pH 10) at (d) 50 mV/s and (e) 500 mV/s scan rate. Turn over frequency (TOF) at pH 10 as a function of applied potential for (c) TEMPO and (f) TEMPO-OCH_3.

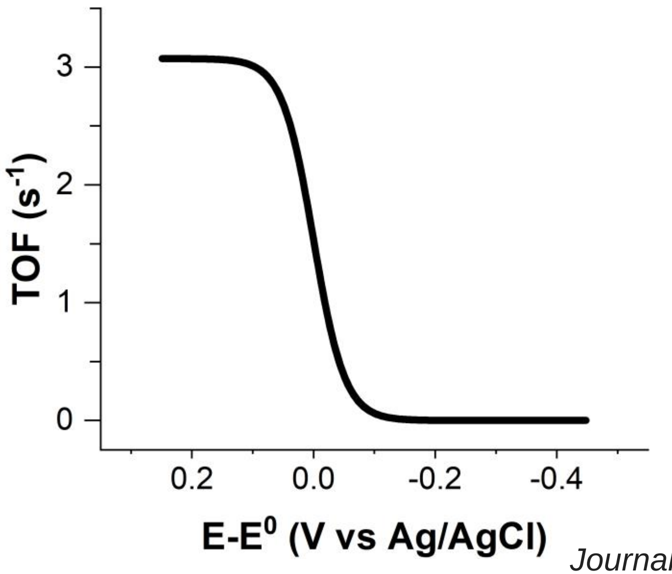
Supplementary Information: TEMPO





$$TOF = \frac{2k_f C_{IPA}^0}{1 + \exp\left(\frac{nF}{RT}\left(E - E^0_{TEMPO^+/TEMPO}\right)\right)}$$





Summary

- Proposed a mechanism for TEMPO mediated IPA oxidation
- Electrocatalysis via TEMPO derivatives is pH dependent
- TEMPO-OCH_3 emerged as the most promising molecular catalyst for converting IPA to acetone
- Will next work on identifying an efficient catalyst for acetone to IPA conversion

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