Compact, Modular, and High-Yield Membrane Reactor for Carbon-Neutral Methanol Synthesis from Direct Air Capture and Carbon-Free H_2 Production

DE-FE0032404

Shoujie Ren, Zhiqin Qiang, *E2H2NANO, LLC*
Mark Swihart, Miao Yu, Lisa Vahapoglu, *University at Buffalo (UB)*
Vijay Ramani, *Washington University in St. Louis (WUSTL)*

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Project Overview

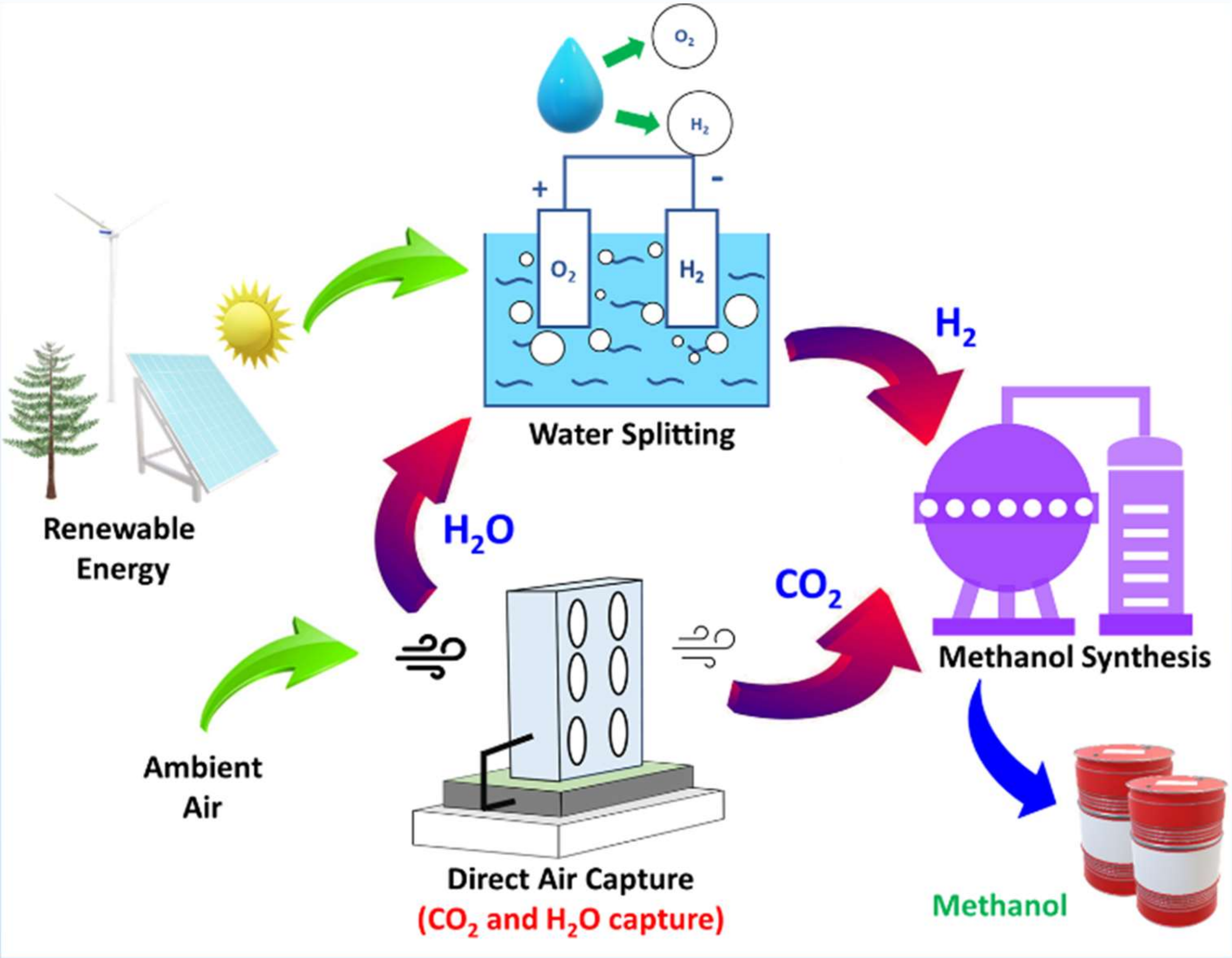
- **Technical Performance Period:** Phase 1, Dec. 20, 2023 - Dec. 19, 2024
- **Total Funding:** $500,000 (DOE: $400,000, Cost share:$ 100,000)
- **Objectives:** 1) conceptually design a compact, modular, and high-yield membrane reactor (MR) process for carbon-neutral methanol synthesis using carbon dioxide (CO_2) from direct air capture (DAC) and carbon-free hydrogen (H_2), 2) demonstrate the feasibility of the integrated process for carbon-neutral methanol synthesis
- **Goal:** to achieve target of <$800/tonne carbon-neutral methanol production
- **Team:**

Member	Roles
E2H2NANO	• Lead on project management and planning • Lead on process design, key components integration, construction, and testing • Lead on techno-economic and life-cycle analyses • Supporting DAC process, carbon-free H_2 production process design, and CBP activities
UB	• Lead on DAC process design, construction, testing, Community Benefits Plan (CBP) activities • Supporting techno-economic and life-cycle analyses
Washington University in St. Louis	• Lead on carbon-free H_2 production process design, construction, and testing • Supporting techno-economic and life-cycle analyses and CBP activities

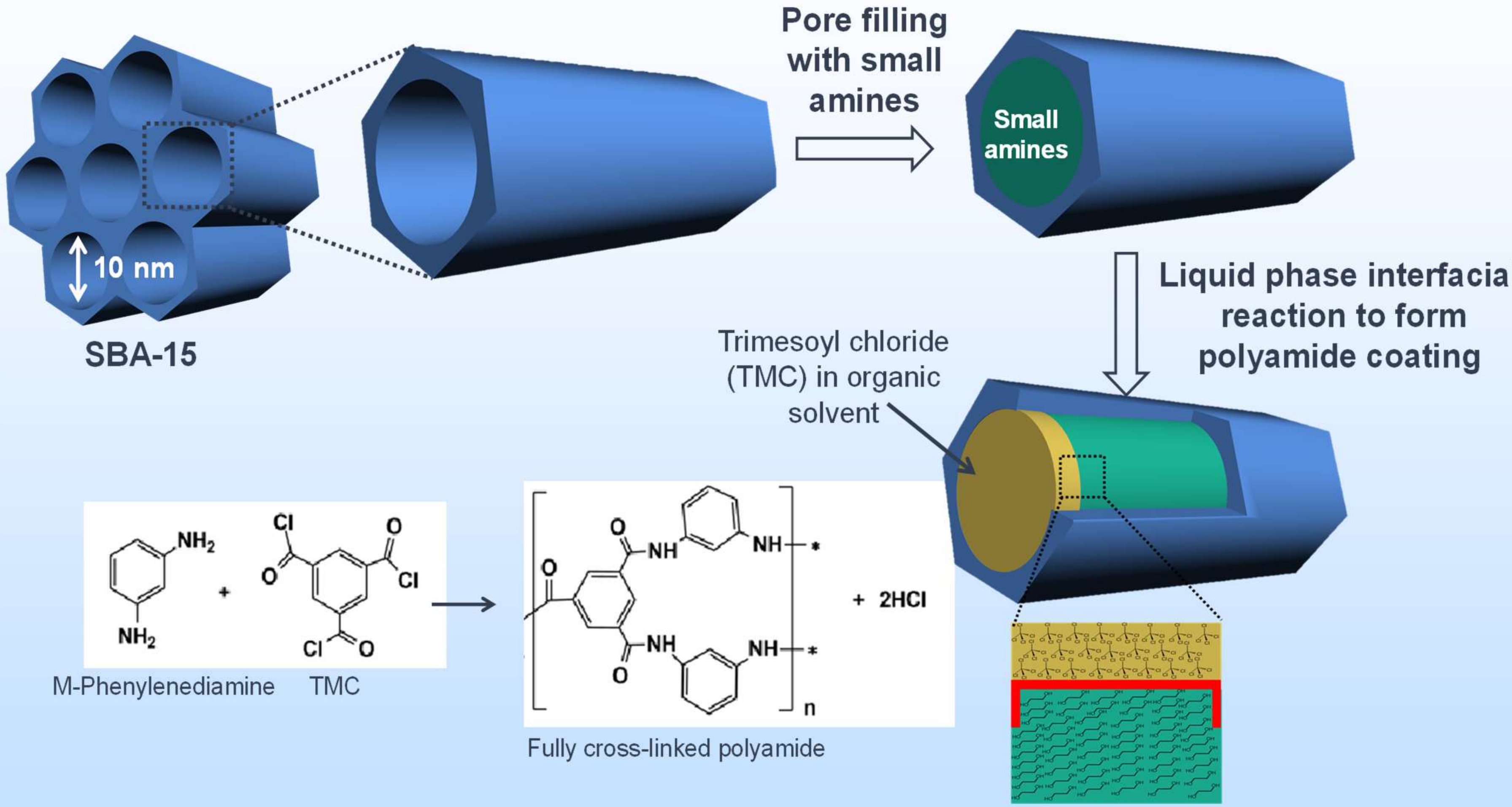
Technology Background

The technology builds on three DOE-supported technologies:

- DAC using trapped small amines in hierarchical nanoporous capsules (DE-FE0031969),
- Carbon-free H_2 production via proton exchange membrane water electrolysis (PEMWE) (DE-SC0007574);
- Transformational membrane reactor (MR) for methanol synthesis from CO_2 and H_2 (DE-AR0000806).



DAC using trapped small amines in hierarchical nanoporous capsules



Dry condition

$$CO_2 + 2RNH_2 \leftrightarrow RNH_3^+ + RNHCOO^-$$

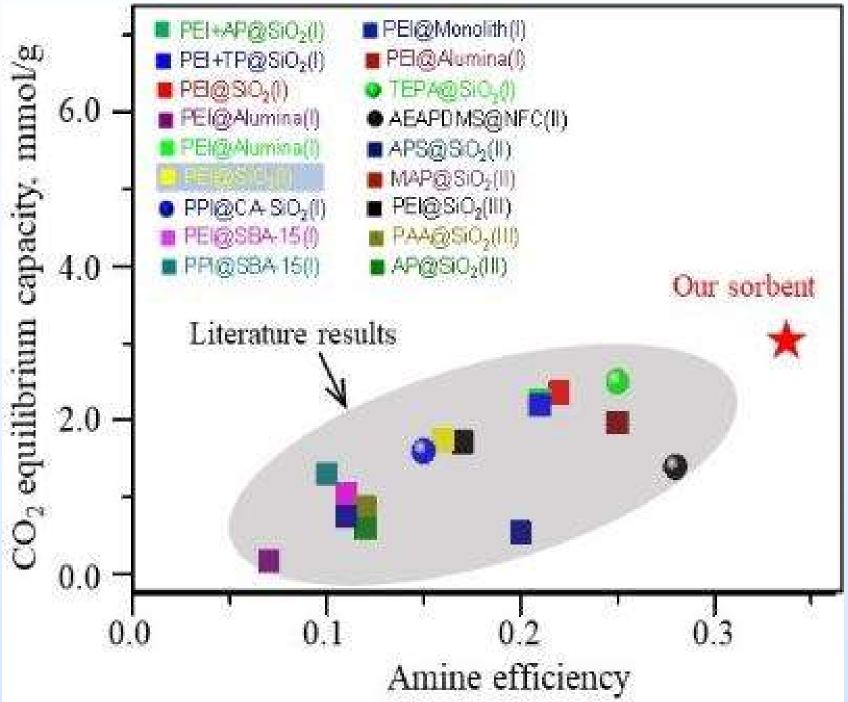
$$CO_2 + 2R_1R_2NH \leftrightarrow R_1R_2NH_2^+ + R_1R_2NHCOO^-$$

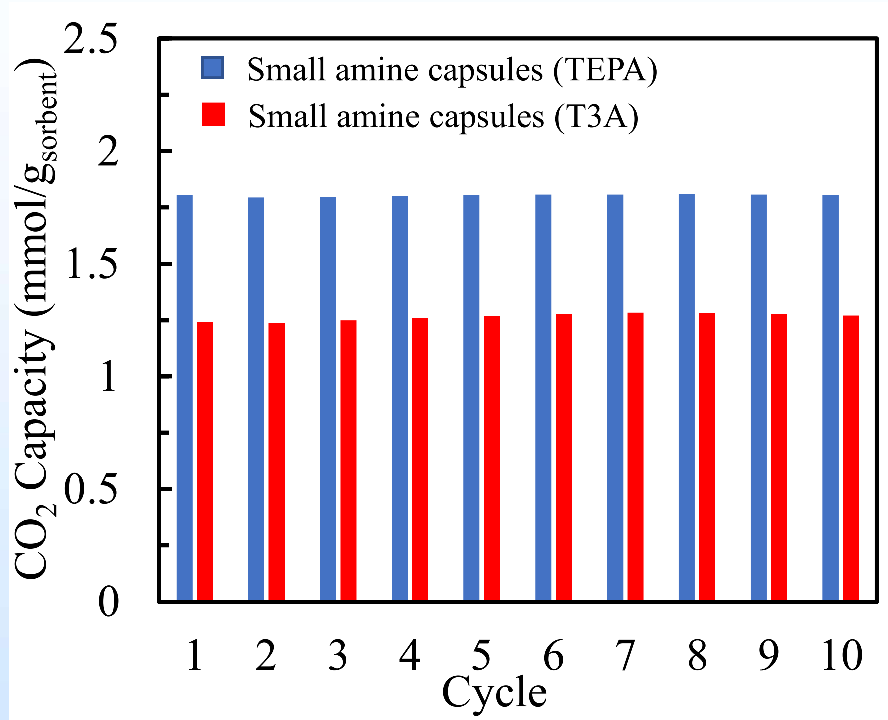
Moisture condition

$$CO_2 + R_1R_2NH + H_2O \leftrightarrow \underset{\text{bicarbonate}}{R_1R_2NH_2{}^+HCO_3{}^-} \leftrightarrow \underset{\text{carbonate}}{R_1R_2NH_2{}^+CO_3{}^{2-}}$$

$$CO_2 + R_1R_2R_3N + H_2O \leftrightarrow R_1R_2R_3NH^+HCO_3{}^- \leftrightarrow R_1R_2R_3NH^+CO_3{}^{2-}$$

Higher amine efficiency, greater CO_2 sorption capacity, and good stability for our DAC sorbents





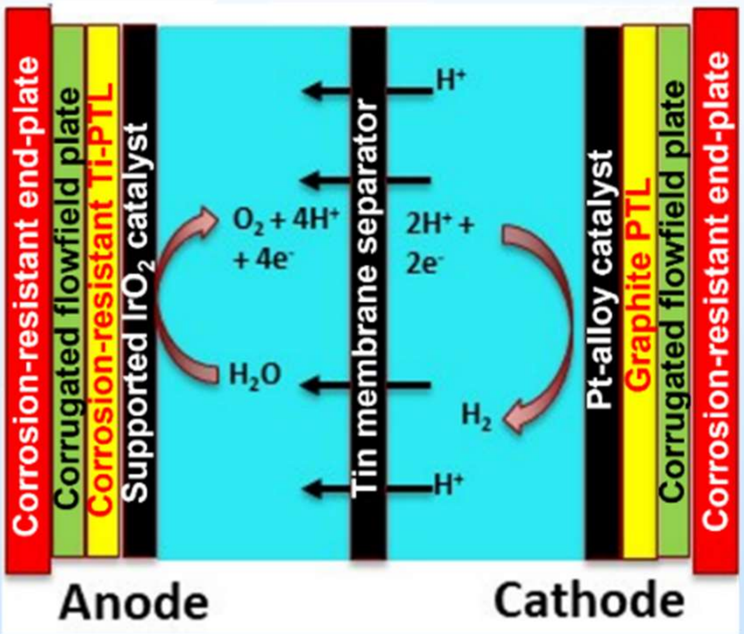
Our sorbent structure has the following features/advantages:

- Fast reaction kinetics, and thus much higher amine efficiency and greater CO_2 sorption capacity than the DAC absorbent materials reported in the literature for dilute CO_2 (~410 ppm) in the air;
- Good sorbent stability because the small amines are sealed inside the capsules;

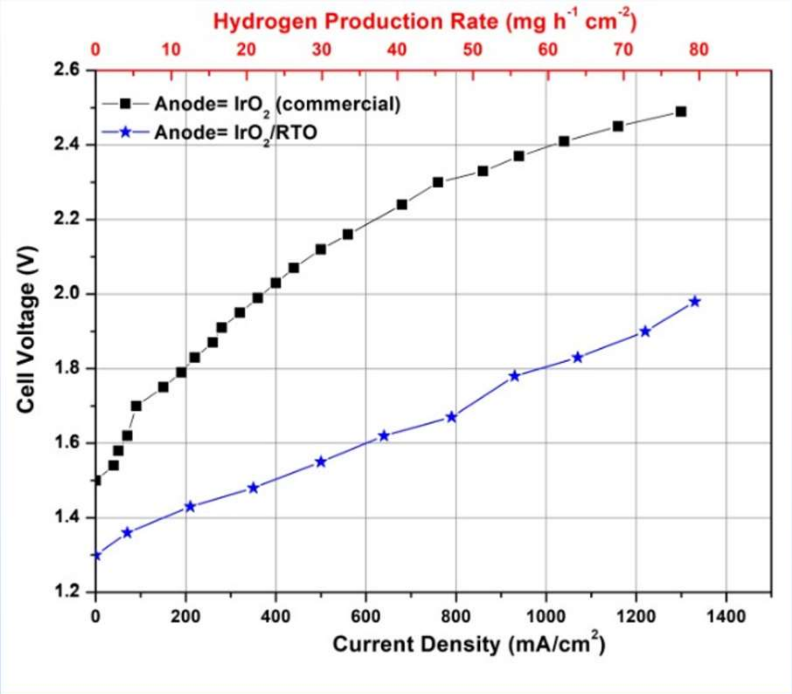
Unique corrosion-resistant supports for IrO_2 electro-catalysts PEMWE for Carbon-free H_2 production

Kinetics of H_2 production is limited by the oxygen evolution reaction (OER) occurring at the anode

The proposed technology for PEMWE



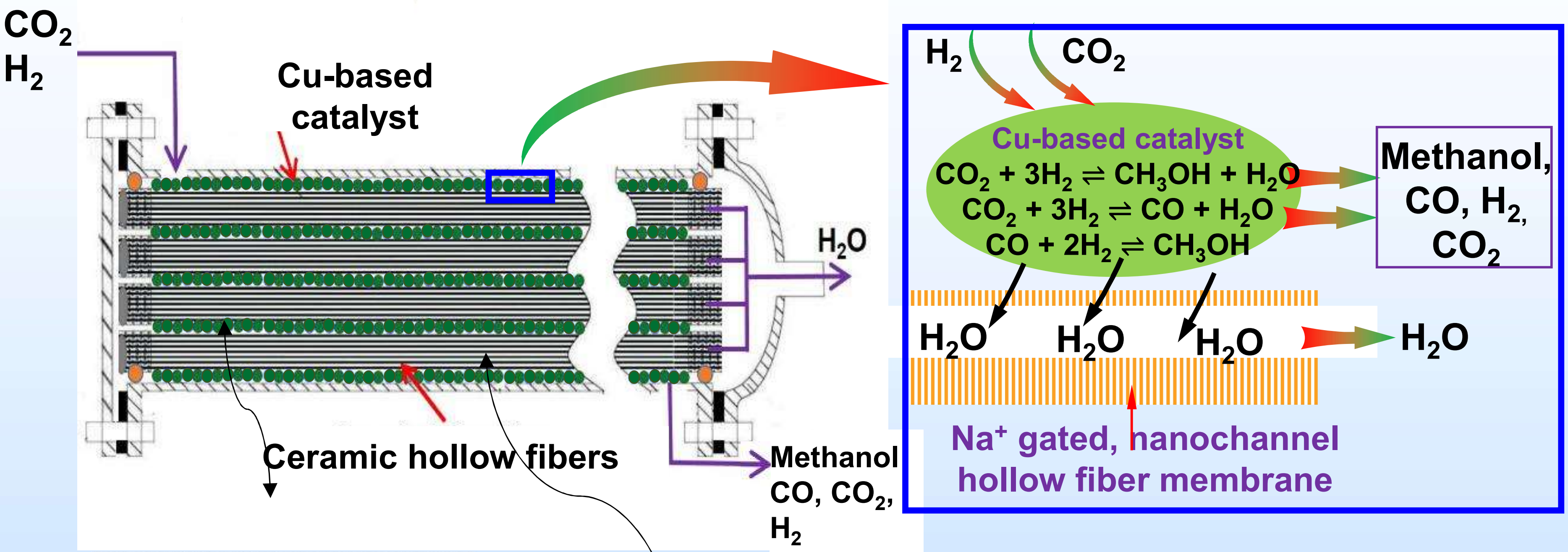
Performance comparison with IrO_2/RTO and commercial IrO_2 as an anode

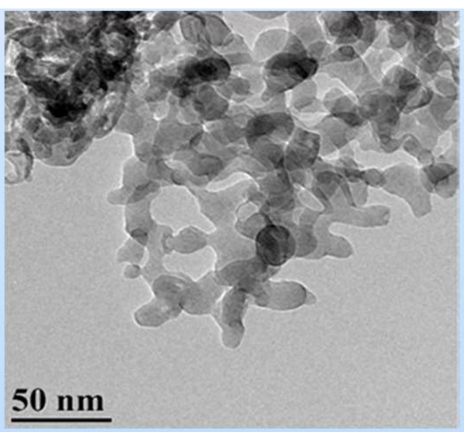


- PEMWE uses unique corrosion-resistant support to yield supported IrO_2 electrocatalysts that allow for excellent durability (> 1,000 hours shown with minimal decay), while achieving high H_2 production rates at lower overpotentials (1.8 V or less total V) by enhancing the efficacy of the OER.

- Proposed PEMWE operates at ~80 ºC producing H_2 at standard pressures up to 35 bar.

High-energy efficient modular MR for one-step, high purity (>99%) methanol synthesis directly from CO_2





Active Cu-based catalyst

Na^+- nanochannel ceramic hollow fiber membrane

Our unique Na+-gated, nanochannel membrane only allows fast water permeation and blocks H_2 and CO_2

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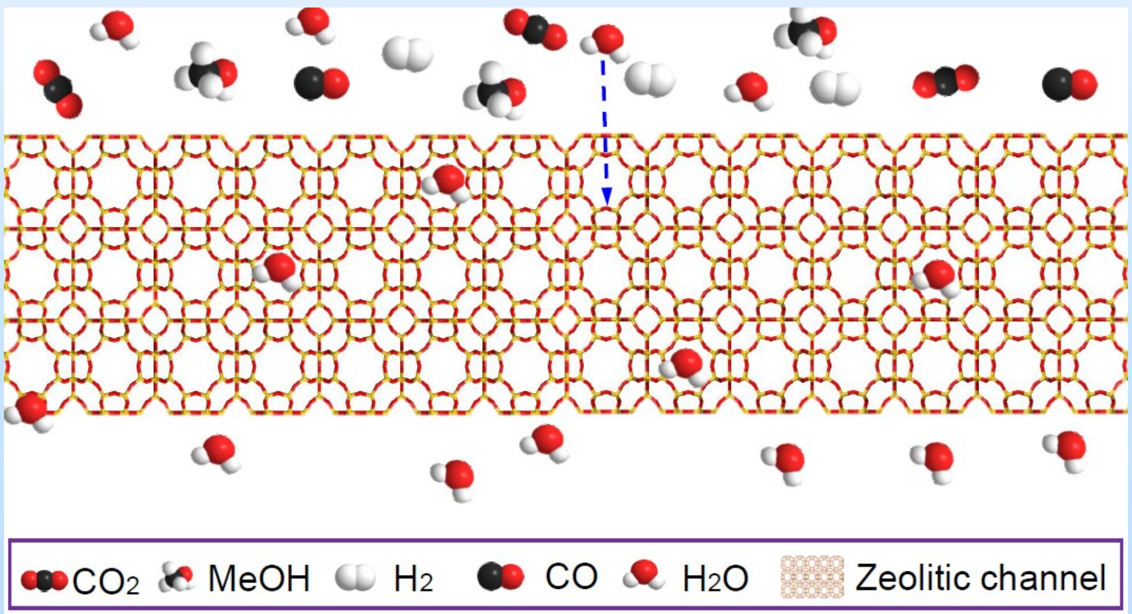
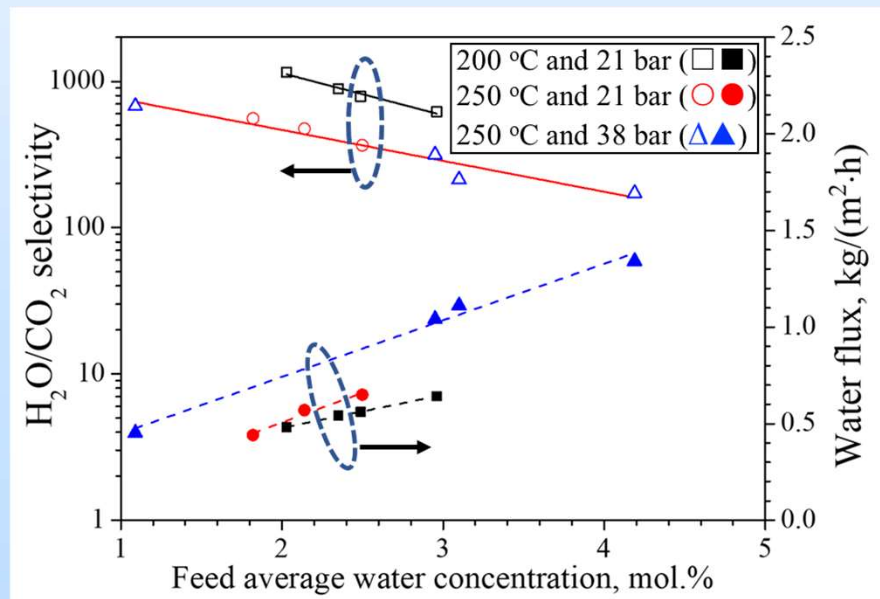
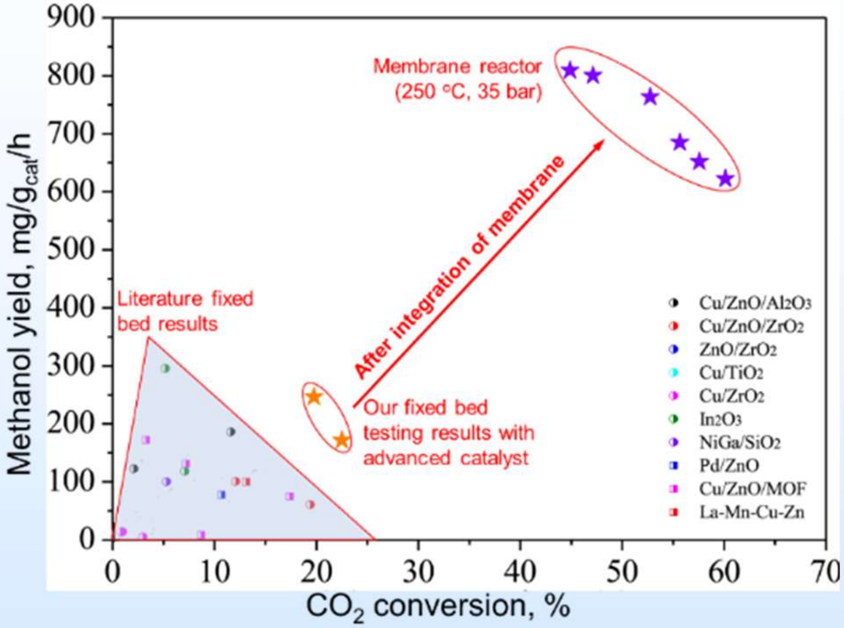
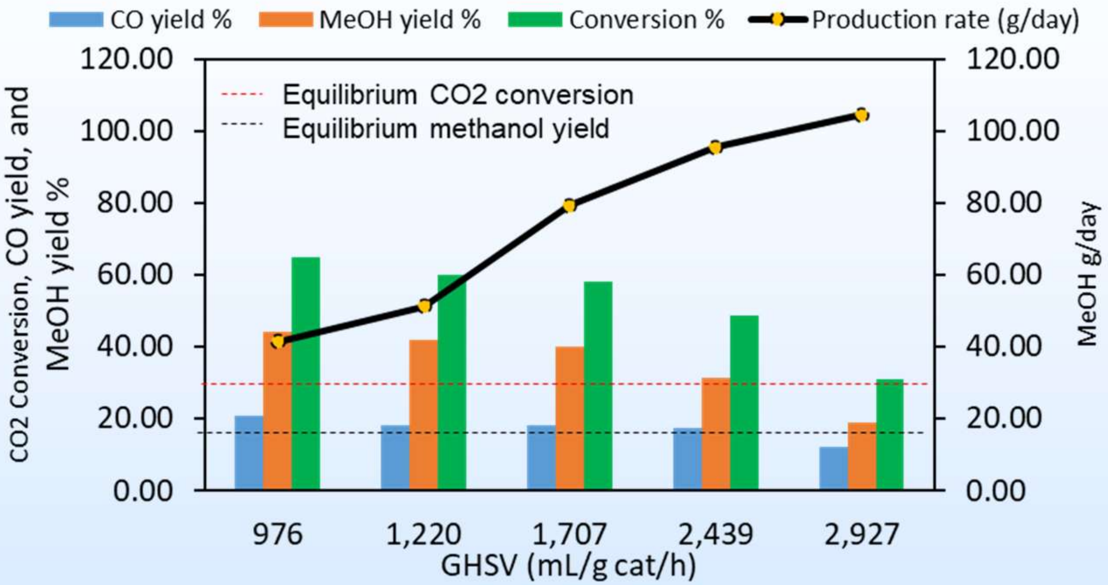
Na^+ neutralizes the negatively charged NaA framework, allowing fast transport of small H_2O molecules (kinetic diameter: 0.26 nm), whereas blocking the permeation of larger molecules, such as H_2 (0.289 nm), CO_2 (0.33 nm), CO (0.38 nm), and MeOH (0.40 nm)

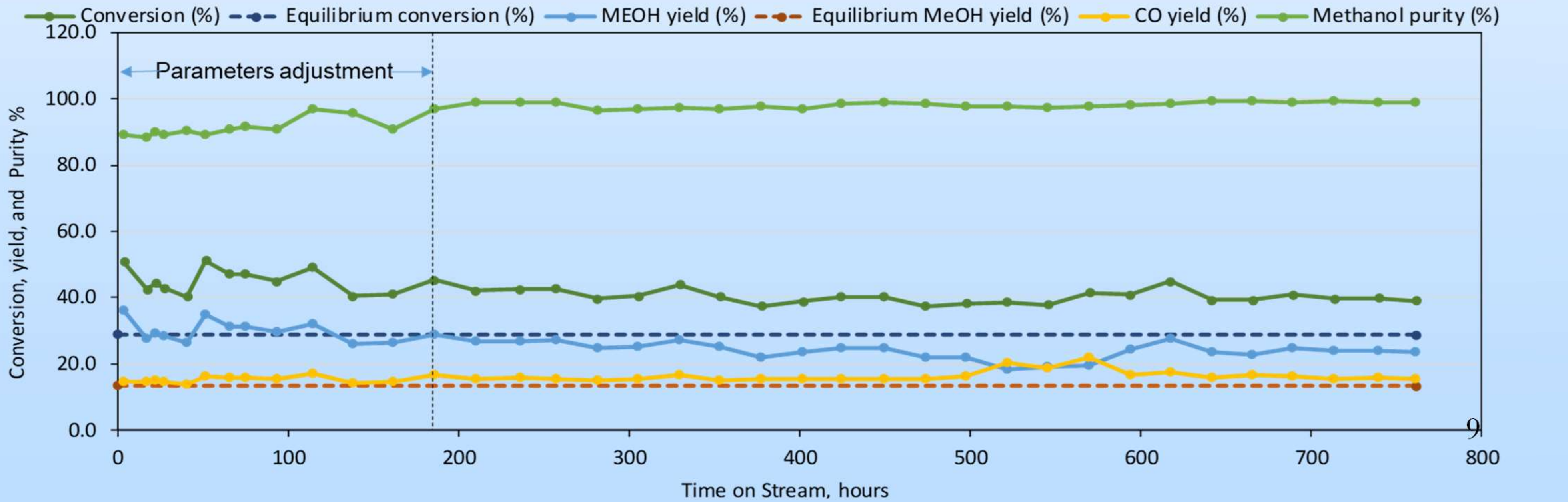




3X CO_2 conversion (>60%) and 3X methanol yield (>40%) with >99% purity, and excellent stability







Technical Approach/Project Scope

Task 1 : Project management and planning

Subtask 1.1 – Project Management Plan

Subtask 1.2 – Technology Maturation Plan

Subtask 1.3 – State Point Data Table

Subtask 1.4 – Preliminary Techno-Economic Analysis (TEA)

Subtask 1.5 - Preliminary Life Cycle Analysis (LCA)

Subtask 1.6 - Technology Gap Analysis (TGA)

Subtask 1.7 - Initial Technology EH&S Risk Assessment

Task 2 - R&D Community Benefits Plan

- Quality Jobs Plan
- Diversity, Equity, Inclusion, and Accessibility Plan
- Justice40 Initiative Plan
- Community and Stakeholder Engagement Plan

Task 3 – Conceptual design

- Block flow diagram identifying all major process equipment for the entire process
- High-level flow diagram of the integrated process with detailed descriptions of each individual component

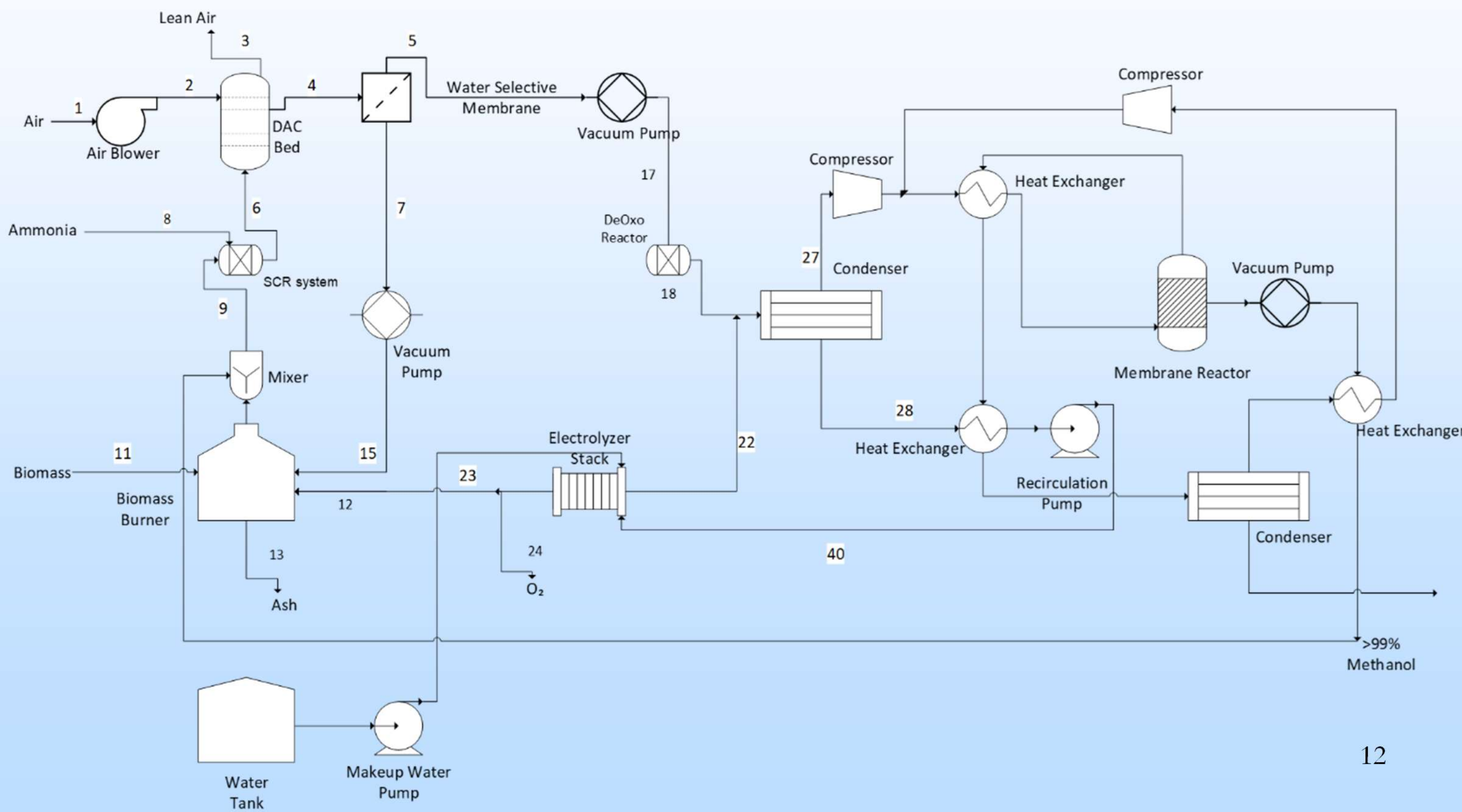
Decision Point	Date	Success Criteria
Go/no-go decision point at (Phase 1 end)	9/19/25	1) Preliminary TEA report submitted to DOE, and the potential of methanol production cost of <$800/tonne demonstrated in the report; 2) Preliminary LCA report submitted to DOE, and the potential of total CO_2 emission < -1.0 t CO_2/tonne methanol demonstrated in the report; 3) ≥2 workshops being organized for underserved communities and researchers from underrepresented groups being involved in the project.

Technical challenges/risks and mitigation strategy

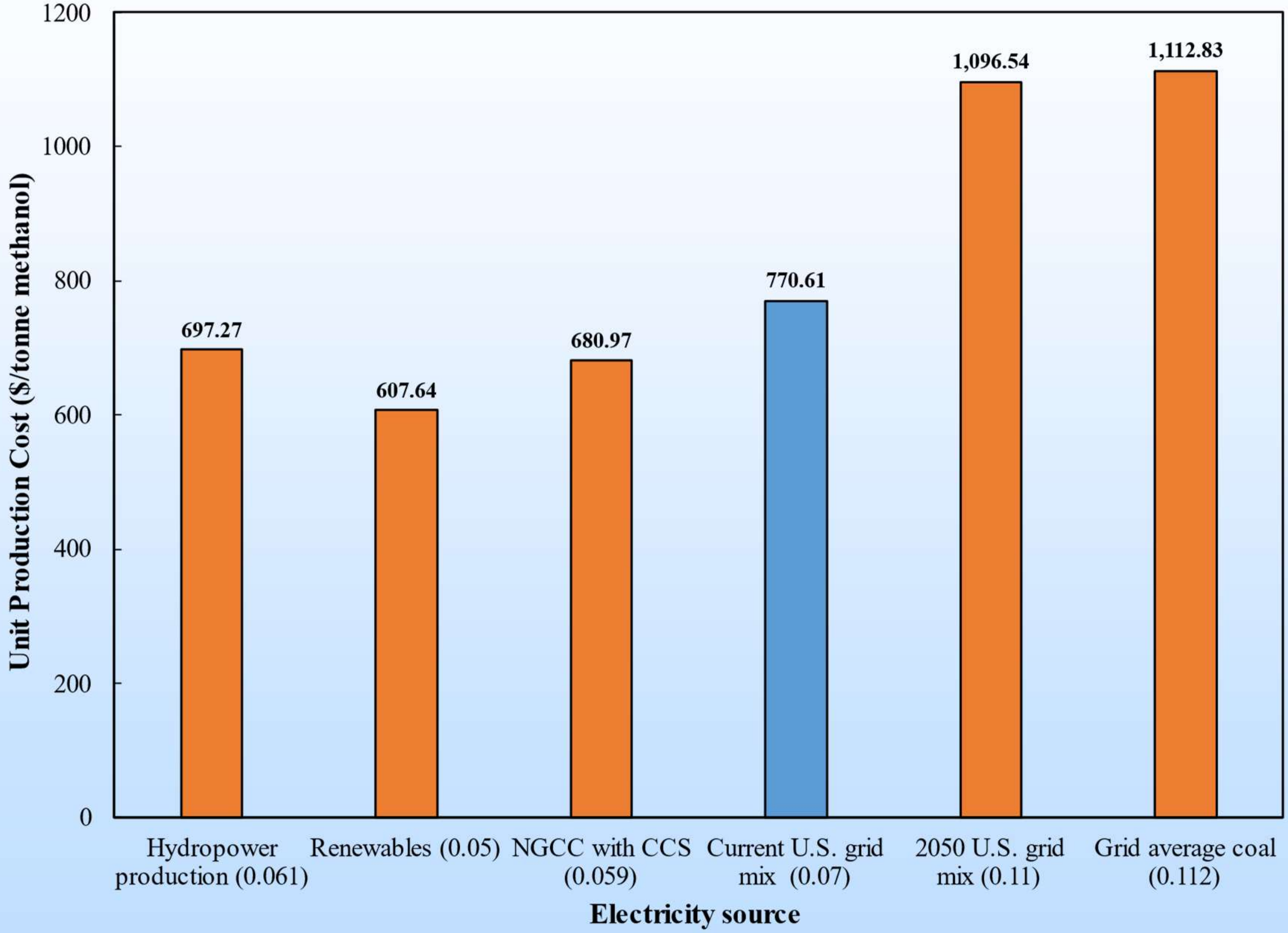
Perceived Risk	Risk Rating			Mitigation/Response Strategy
	Probability	Impact	Overall	
	Low, Medium (Med), High			
Technical/Scope Risks:				
DAC system: CO_2 capacity not sufficiently high or kinetics not fast enough	Low	High	Low	1) Increase amine loading; and 2) decrease coating thickness to allow faster diffusion
DAC system: sorbent regeneration energy higher than expected	Low	Med	Low	1) Optimize operating conditions; and 2) optimize sorbent regeneration process design
H_2 production system: catalyst usage not sufficiently high	Med	High	Med	1) Disperse catalyst onto high surface area substrates; and 2) improve substrate conductivity
Methanol synthesis system: yield and purity not sufficiently high	Low	High	Med.	1) Optimize operating conditions; and 2) optimize membrane reactor process design
Operating conditions of three components do not match well in integrated system	Med	Med	Med	1) Process simulation will be conducted to have better integration; and 2) necessary compression/depressurization and/or cooling/heating will be considered
Unsatisfied energy efficiency of the integrated system	Med.	high	Med.	1) Seek further integration between 3 components; and 2) improve energy efficiency for each component
Cost/Schedule Risks:				
Delay of tasks	Low	Low	Low	Early and frequent meetings will be held to avoid delay of tasks. The project team will monitor the staffing/equipment needs closely.
Financial Risks:				
The shortfall of cost share	Low	Low	Low	E2H2NANO, UB, and WUSTL are committed to providing the required cost share.
ES&H Risks:				
Environmental, health, and safety during testing	Low	High	Low	Hazard assessments for test operations will be conducted during design phase.

Progress and Current Status of Project

Process flow diagram for the integrated system

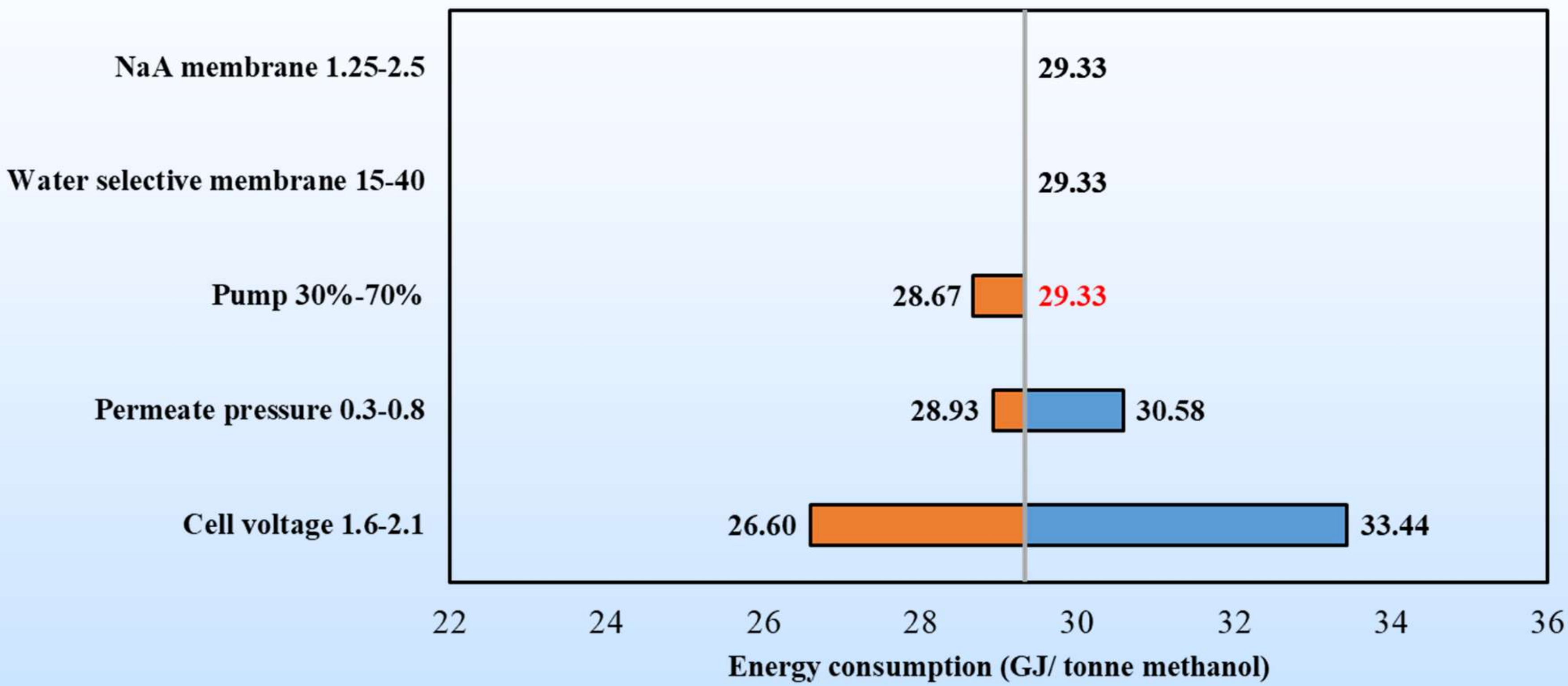


TEA: $771/tonne methanol using grid mix and $608/tonne methanol using renewables



- The unit production cost is $771 /tonne methanol with the current grid mix and $608 /tonne methanol with renewables, both below the $800/ /tonne methanol target.

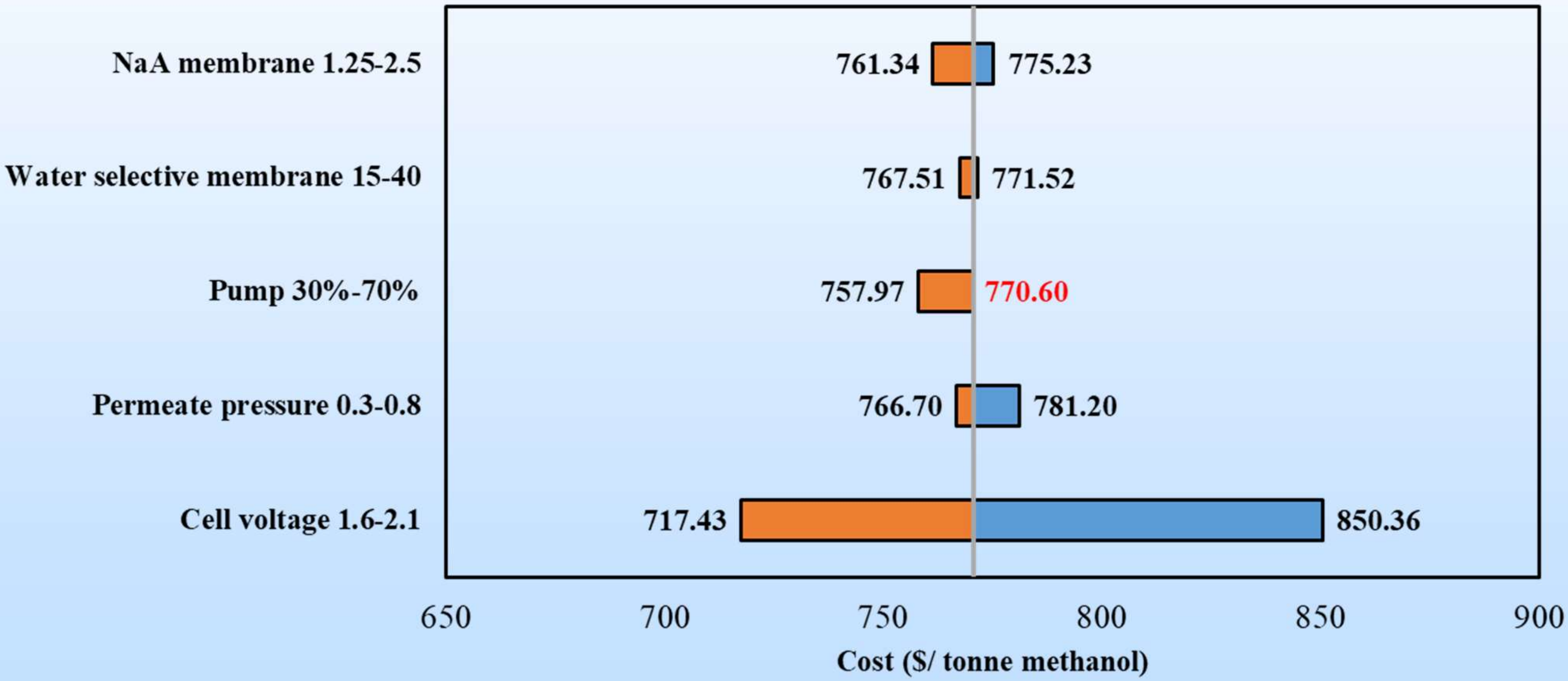
TEA-Energy consumption: Cell voltage and permeate pressure most impactful factors



- Most of the energy is consumed by the electrolyzer of the whole integrated system, so the cell voltage becomes the most sensitive parameter for TEA energy consumption and cost.
- Increasing pump efficiency and permeate pressure can reduce energy consumption and cost.
- NaA membrane and water selective membrane flux will not affect the energy consumption

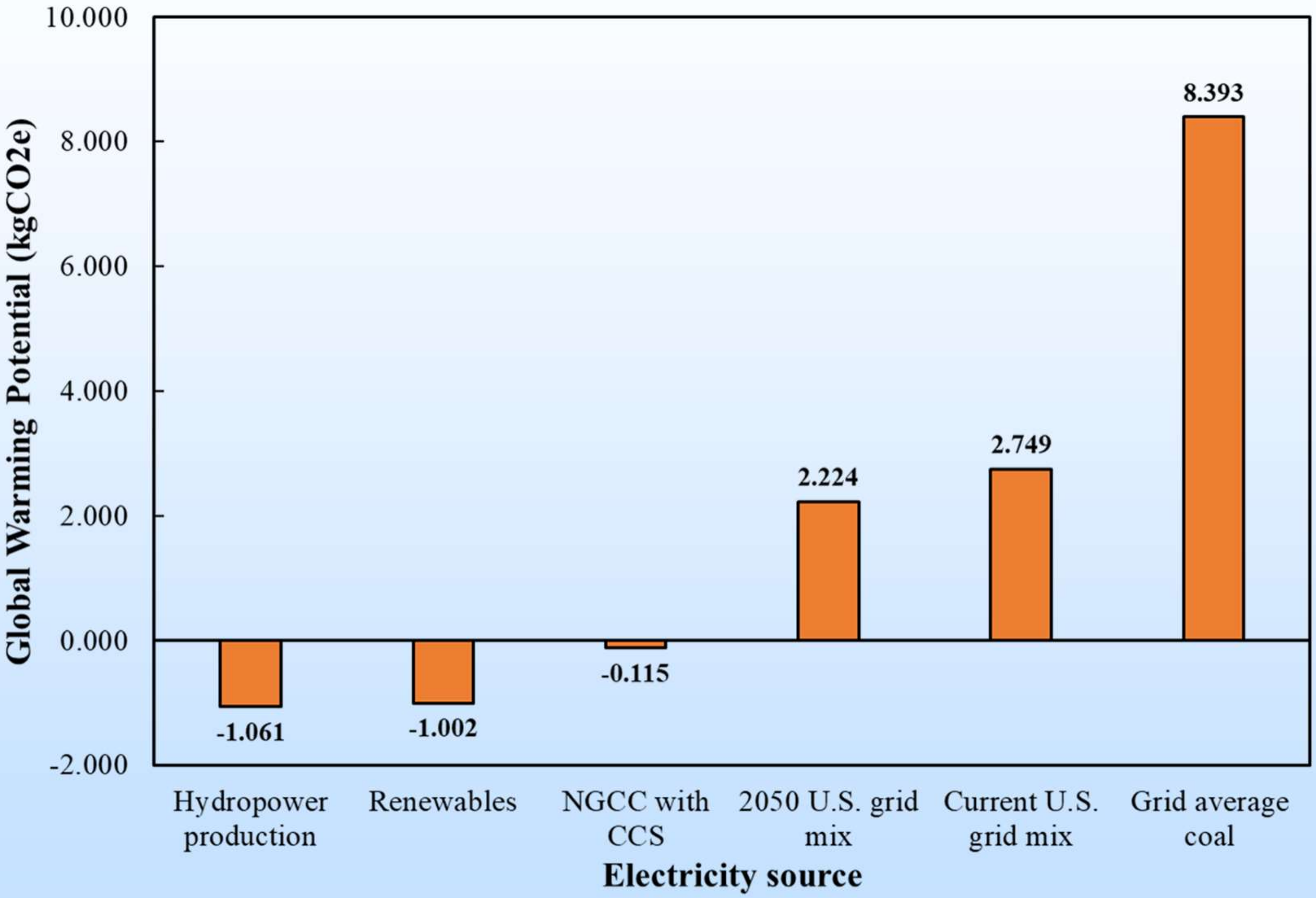
TEA-methanol production cost: cell voltage, pump efficiency, permeate pressure, NaA membrane flux key factors

- NaA membrane flux: 1.5 kg/ m^2 h
- Water selective membrane flux : 20 kg/ m^2 day
- Pump efficiency: 30%
- Permeate pressure: 0.6 bar
- Cell voltage :1.8 V
- Electricity rate: 0.07 $/kWh (National Grid)



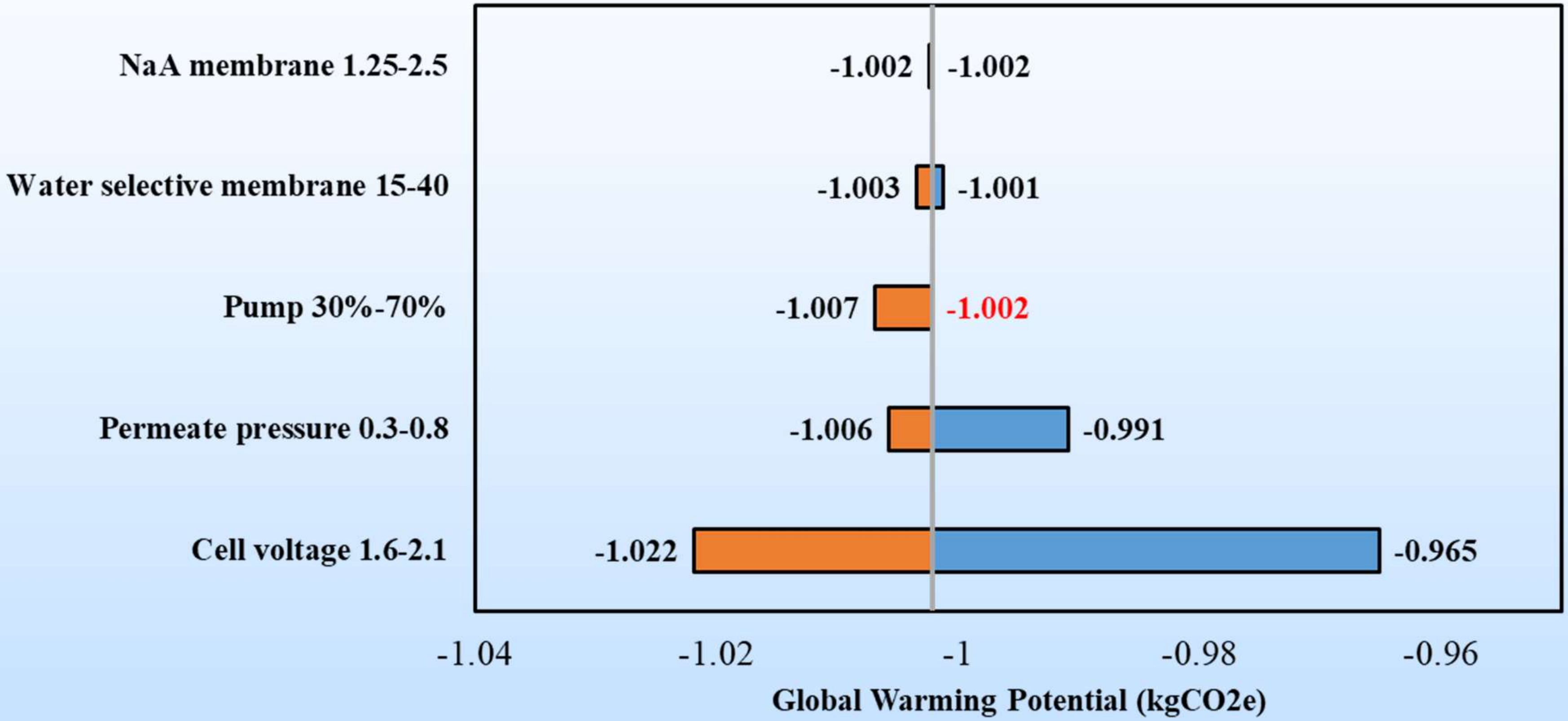
- Reduce cell voltage, increase pump efficiency, and optimize permeate pressure can significantly lower unit production costs.
- Improving NaA membrane flux contributes to cost reduction

LCA: negative carbon emission with GWP ≤-1.002 t CO_2/tonne methanol produced



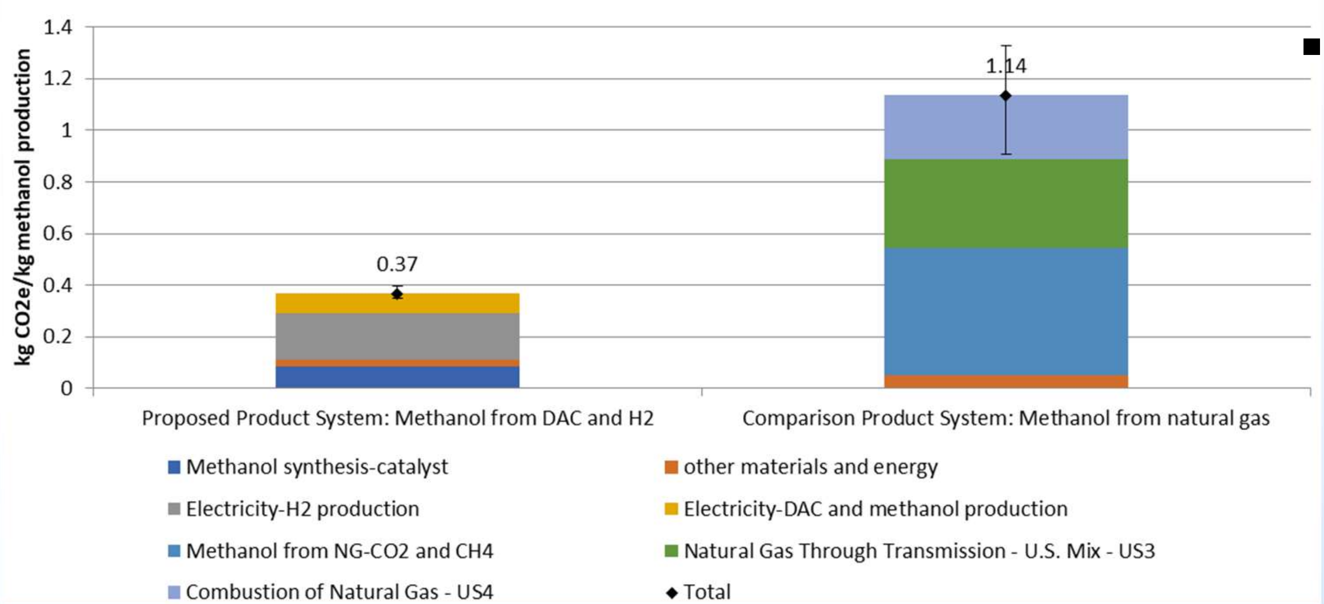
- Hydropower and renewable energy sources have the lowest impact on global warming potential (GWP), with CO_2 emissions of -1.061 kgCO2e and -1.002 kgCO2e per kg methanol production.

Cell Voltage, permeate pressure are most sensitive parameters for GWP



- Cell voltage is the most sensitive parameter for methanol production.
- NaA membrane and water selective membrane flux have minimal influence on the greenhouse gas (GHG) emissions of the integrated system.

Our technology 68% lower CO_2 emission than natural Gas-based methanol production



- The integrated system's GWP impact is only 32% of that of the natural gas-based system, representing a **68%** reduction in GWP (excluding the CO_2 captured from DAC, which has a -1.374 kgCO2e per kg methanol production)

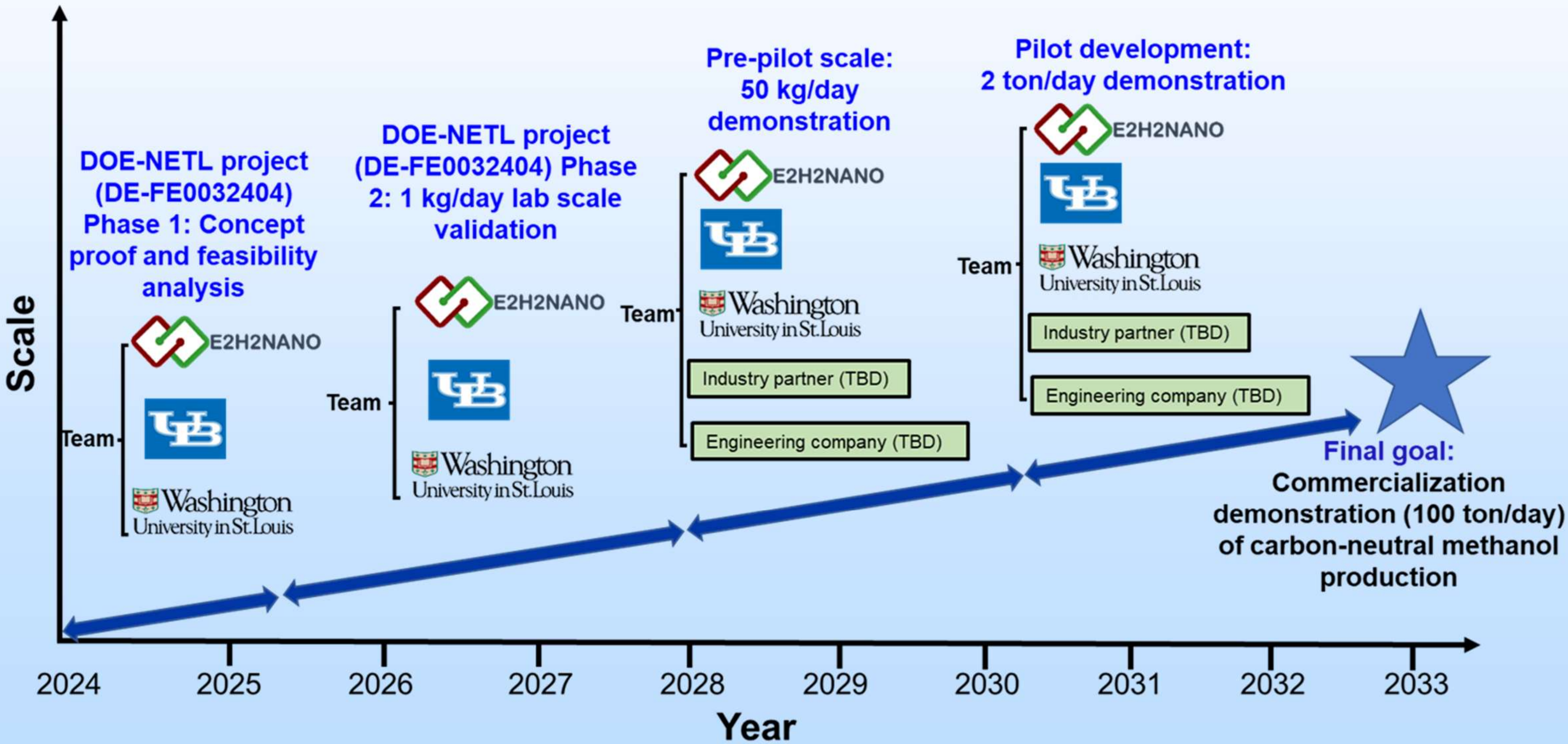
Impact Category	Our technology	natural Gas-based methanol production	Unit
Photochemical Smog Formation Potential - TRACI 2.1 (NETL)	0.01226	0.09358	kg O_3e
Acidification Potential - TRACI 2.1 (NETL)	0.00104	0.00268	kg SO_2e
Water Consumption (NETL)	3.21823	1.22723	kg
Global Warming Potential [100 yr] - TRACI 2.1 (NETL)	-1.002	1.13507	kg CO_2e
Ozone Depletion Potential - TRACI 2.1 (NETL)	1.56E-11	8.40E-12	kg CFC-11e
Particulate Matter Formation Potential - TRACI 2.1 (NETL)	1.00E-04	3.65E-05	kg $PM_{2.5}$e
Eutrophication Potential - TRACI 2.1 (NETL)	3.81E-05	1.97E-04	kg Ne

Summary of Community Benefits Plan

- Prepare student assistant job descriptions for advanced undergraduate students and graduate students from STEM and recruit a URM engineer or technician
  - ✓ Two female master students from UB have been recruited as technicians working on the project since January.
  - ✓ Three more female undergraduates were recruited as interns working on the project starting end of May and early of June.
- Completed an evidence-based implicit bias training for key personnel on 6/12/2024.
- Phase 2 project site has been preliminarily identified in Buffalo, NY and we are working on identifying beneficiary communities and developing R&D CBP.
- The contents for 2 workshops for underrepresented and First-Generation college students at UB have been developed and the workshops will be offered in late September and October.

Plans for future development

Technology Development Path



Summary Slide

- Process design for the integrated system including DAC with sorbents, carbon-free hydrogen production by PEM water electrolysis, and methanol synthesis by membrane reactor has been completed and TEA and LCA models have been created.
- TEA shows methanol production costs are $771/tonne methanol using grid mix and $608/tonne methanol using renewables
- TEA sensitivity analysis indicates that cell voltage and permeate pressure most impactful factors for energy consumption and cell voltage, permeate pressure, and Na^+-membrane flux for most impactful factors for production cost.
- LCA shows our technology has negative carbon emission with GWP ≤-1.002 t CO_2/tonne methanol produced, and cell Voltage and permeate pressure are most impact parameters for GWP.
- Our technology has 68% lower CO2 emission than natural gas-based methanol production

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