

**Environment and Natural Resources Trust Fund**

# 2023 Request for Proposal

## **General Information**

**Proposal ID:** 2023-076

**Proposal Title:** Converting Post-Combustion CO2 to Green Butanol Fuel

## **Project Manager Information**

**Name:** Sam Toan

**Organization:** U of MN - Duluth

**Office Telephone:** (218) 726-8759

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## **Project Basic Information**

**Project Summary:** To mitigate greenhouse gas (GHG) emissions in Minnesota, we propose to convert post-combustion CO2 to green butanol fuel via a novel CuP2/3D graphene catalyst

**Funds Requested:** $421,000

**Proposed Project Completion:** June 30, 2025

**LCCMR Funding Category:** Air Quality, Climate Change, and Renewable Energy (E)

## **Project Location**

**What is the best scale for describing where your work will take place?** Region(s): NE

**What is the best scale to describe the area impacted by your work?** Statewide

**When will the work impact occur?** In the Future

## **Narrative**

**Describe the opportunity or problem your proposal seeks to address. Include any relevant background information.**

Power generation from fossil fuels remains the most reliable method for electricity generation, making up more than 80% of the global energy supply. However, fossil fuel combustion generates over 25% of CO2 emissions. The unsustainable utilization of fossil fuels has led to a global energy crisis and increasing atmospheric CO2, which breaks the natural carbon cycle and exacerbates the climate crisis. Accordingly, capturing, storing, and utilizing CO2 is attracting tremendous attention. Flue gas treatments that capture and convert CO2 emissions to green fuels, like butanol, are vital in addressing the climate crisis while meeting future energy demands.
CO2 is an ideal feedstock to achieve green fuel production goals since it is a high-volume greenhouse gas (GHG). Electrochemical CO2 reduction processes convert CO2 into value-added products and green fuels. Although precious metals, such as silver and gold, exhibit superior CO2 reduction selectivity, they are unsuitable for CO2 conversion to green fuels because of their high cost and questionable stability. Therefore, designing low-cost, stable electrocatalysts for CO2 reduction is crucial to enabling efficient production of green butanol from CO2.

**What is your proposed solution to the problem or opportunity discussed above? Introduce us to the work you are seeking funding to do. You will be asked to expand on this proposed solution in Activities & Milestones.**

Unstable homogeneous catalysts for hydrogenating CO2 to butanol require harsh conditions. Consequently, developing heterogeneous catalysts for CO2 conversion is challenging. We propose to control the structure of 3D graphene (3DG) electrodes and build a copper diphosphide (CuP2) nanocluster/3DG composite material, where the 3DG spatial network limits the growth of Cu nanoparticles and prevents aggregation. This project will reveal the relationship between the microstructure and the electrocatalytic performance of CuP2/3DG composites and clarify the design principles of new composite electrode materials to achieve efficient activation and selective catalytic conversion of CO2 to butanol under mild conditions. The results will provide a scientific basis for the efficient and economical conversion of flue gas CO2 to green butanol.

Enhancing CO2 adsorption on the 3DG surface improves the density and speed of charge transfer between the CuP2 catalyst and CO2 to achieve a stable electrocatalytic conversion. We propose the following activities to demonstrate the production of green butanol fuel from CO2:

1. Develop 3DG for CO2 reduction using alkali-metal chemistry.
2. Characterize size-confined CuP2 nanoclusters in 3DG.
3. Accelerate CO2 electrochemical activation at the interface reaction.
4. Conduct life cycle assessments (LCA) of the process.
5. Simulate the CO2 electrochemical catalytic reduction.

**What are the specific project outcomes as they relate to the public purpose of protection, conservation, preservation, and enhancement of the state’s natural resources?**

As a clean energy, butanol is one of the best replacements for fossil fuels. Minnesota is one of the pioneering states in the US for promoting green alternative fuels such as ethanol and butanol, especially since butanol can be a direct substitution for fossil fuel-based gasoline. Removing CO2 from industrial sources or the atmosphere, coupled with cutbacks in fossil fuel use effectively relieves the dual pressures on Minnesota’s environment and resources.

## **Activities and Milestones**

### **Activity 1: Develop 3DG and nitrogen-doped 3DG with selected features from the reduction of CO2 via the alkali-metal chemistry-based strategy.**

**Activity Budget:** $105,279

**Activity Description:**Since graphene should have large surfaces for charge accumulation, hierarchical pore structures for transferring electrolyte ions, and continuous 3D frameworks for electron transportation, we will synthesize structured 3D graphene (3DG) by reacting CO2 with alkaline metals (Na, K, Mg) for novel morphologies, enhanced surfaces, and optimal pore structures using temperature and reaction time controls. This eliminates complicated graphene exfoliation, self-assembly, and surface activation perforation, resulting in 3DG with commercially-desirable morphologies and self-supporting structures for CuP2 nanocluster catalysts.
Nitrogen doping by heat treatment places graphene derivatives in a tube furnace using nitrogen/ammonia as sources. Compared with non-metal heteroatoms, nitrogen’s size is close to carbon and more compatible with graphene’s lattice structures. Hence, nitrogen can be more easily doped into the lattices, producing a more stable 3D nitrogen-doped graphene (3DNG). The lattice-nitrogen, compared with carbon, will have one more electron that can enter the conduction band and open the graphene bandgap, thereby obtaining an n-type nitrogen-doped graphene (N-graphene, NG) semiconductor. Nitrogen doping can generate active regions in the graphene lattice and improve CO2 catalytic reduction performance. The presence of nitrogen is also conducive to the attachment and fixation of metal/metal oxide nanoparticles, preventing desorption from the graphene surface or agglomeration.

**Activity Milestones:**

|  |  |
| --- | --- |
| **Description** | **Completion Date** |
| Fabricate 3DG with high surface area, porous structure, and nitrogen doping. | December 31, 2023 |
| Evaluate the structure, composition, and support of 3DG and 3DNG for converting CO2 to butanol. | June 30, 2024 |

### **Activity 2: Grow size-confined CuP2 nanoclusters in 3DG frameworks and identify their catalytic applications.**

**Activity Budget:** $105,279

**Activity Description:**Our goal is to develop an in-depth understanding of the precise synthesis and regulation of CuP2 nanocluster (NC) active centers and reveal the dynamic evolution mechanism of NCs.
NCs with sizes ranging from a dozen to a few hundred atoms hold potential in catalysis due to their unique geometric and electronic structures compared to conventional catalysts. 3DG has a controllable pore structure, high specific surface area, and excellent conductivity for supporting a catalyst. The encapsulation of CuP2 nanoclusters with sizes ranging from several to tens of atoms in 3DG exhibits high activity and conductivity for CO2 conversion. We will adopt the direct reaction of active alkali metals and CO2 to prepare 3DG with the unique surface microporous structure at a low cost, further growing size-confined CuP2 nanoclusters in graphene frameworks. Then, various characterization methods will determine the crystal phase, crystal type, structure morphology, composition, specific surface area, and CO2 adsorption capacity. We will also evaluate the electric catalytic reduction of flue gas CO2 to produce butanol products. Further adjustments will be made to optimize the material synthesis method based on the obtained characterization and results of the performance tests.

**Activity Milestones:**

|  |  |
| --- | --- |
| **Description** | **Completion Date** |
| Prepare a 3DG-supported CuP2 NC composite catalyst. | December 31, 2023 |
| Evaluate the electrocatalytic effect of the catalyst. | June 30, 2024 |
| Summarize the structure-activity relationship between the microstructure and the electrocatalytic performance of CuP2/3DG composite materials. | December 31, 2024 |

### **Activity 3: Promote electrochemical activation of CO2 and accelerate the reaction at the electrochemical interface.**

**Activity Budget:** $105,279

**Activity Description:**Since butanol can be separated in the continuous reactor under heating, electrocatalysis should also be coupled with photo- and thermo-catalysis to achieve considerable reaction conversion and rates. The synergistic effect of CO2 electrochemistry activation and thermal field should promote high catalytic performance and improve the economic viability of the catalytic conversion.

Solid oxide electrolysis cells (SOEC) provide a reaction platform to convert CO2 into chemical substances through thermally-coupled electrocatalysis, as demonstrated in the oxygen ion conductive electrolyte membrane SOEC. Under the effect of heat coupling electrocatalysis, the thermo-coupled catalytic electrolytic cell will be used to explore the promotion mechanism of the heat-electricity synergistic catalytic conversion of CO2 through complementary kinetic energy. The ideal strategy for converting CO2 into high-value butanol products uses SOEC with a proton-conducting electrolyte membrane at moderate temperatures (100-300°C). Thus, we will apply the previously-synthesized advanced catalysts to build a robust electrochemical interface to promote C-C coupling and increase the selectivity of CO2 conversion to butanol products, while simultaneously inhibiting carbon deposition. We will also study the surface and interface microstructure of electrode catalysts and use a variable temperature reactor to explore the impact of temperature on catalysis.

**Activity Milestones:**

|  |  |
| --- | --- |
| **Description** | **Completion Date** |
| Design and optimize SOEC; reliability testing. | December 31, 2023 |
| Investigate the effect of temperature on the electrocatalytic reduction of CO2. | June 30, 2024 |
| Summarize the design strategies of the SOEC and the electro-thermal coupling mechanism. | December 31, 2024 |

### **Activity 4: Conduct a preliminary life cycle assessment (LCA) of the new CO2 capture system to determine potential environmental impacts.**

**Activity Budget:** $27,155

**Activity Description:**A preliminary life cycle assessment (LCA) will be conducted to determine the potential life cycle environmental impacts of the new CO2 capture system. The LCA will be modeled using SimaPro v9.1.1 software. The LCA will follow International Organization for Standardization (ISO) guidelines for the overall LCA framework. The system boundary will be established around a representative functional unit (e.g., mass of CO2 captured or mass/volume of butanol produced). We will then establish an inventory of all material flows, emissions, and resource consumption and describe, characterize, and aggregate these elementary flows for different environmental aspects. Primary life cycle inventory (LCI) data will be collected from the laboratory-scale CO2 capture experiments. Secondary data will be collected from peer-reviewed literature, subject matter experts, and established LCI databases, including DATASMART and Ecoinvent v3.6. Environmental impacts will be assessed using the LTS Method, which translates the LCI data into environmental impacts on Human Health, Ecosystems, Resources, Cumulative Energy Demand, Climate Change (100-year time horizon), and Water Use impact categories. Ultimately, this LCA will identify environmental “hot spots” to guide the future pilot-scale development and demonstration of the technology.

**Activity Milestones:**

|  |  |
| --- | --- |
| **Description** | **Completion Date** |
| Complete life cycle inventory of the CO2 capture process. | December 31, 2023 |
| Build an LCA model of the CO2 capture process. | June 30, 2024 |
| Conduct a life cycle impact assessment to determine potential environmental impacts of the process. | December 31, 2024 |

### **Activity 5: Conduct an Aspen Plus process simulation of the proposed electrochemical catalytic reduction of CO2.**

**Activity Budget:** $78,008

**Activity Description:**The overall post-combustion CO2 reactive capture and purification process will be simulated in the Aspen Plus chemical process simulator with fluid- and solid-phase interaction models. This work will inform the economic analysis of the technology, the scale-up of the technology for implementation on a demonstration scale, and process analysis and optimization for determining critical operating conditions to minimize cost and energy requirements and maximize the efficiency of CO2 conversion to butanol. Process simulations will also guide integration of the technology with existing butanol production and purification processes.

**Activity Milestones:**

|  |  |
| --- | --- |
| **Description** | **Completion Date** |
| Simulate the CO2 capture technology. | March 31, 2025 |
| Analyze and optimize the CO2 capture process. | June 30, 2025 |

## **Project Partners and Collaborators**

|  |  |  |  |
| --- | --- | --- | --- |
| **Name** | **Organization** | **Role** | **Receiving Funds** |
| Richard Davis | University of Minnesota Duluth | Co-PI | Yes |
| Matthew Aro | University of Minnesota Duluth | Co-PI leading life cycle assessment (LCA) modeling | Yes |

## **Long-Term Implementation and Funding**

**Describe how the results will be implemented and how any ongoing effort will be funded. If not already addressed as part of the project, how will findings, results, and products developed be implemented after project completion? If additional work is needed, how will this work be funded?**Research into butanol production from CO2 has received worldwide attention. It is an effective way to relieve the dual pressures on the environment and resources in Minnesota. If the proposed work is successful, we believe that to advance the technology to commercialization, our work can receive substantial financial support from governmental agencies (such as the US Department of Energy) and commercial enterprises. The proposed project has also gained support from collaborators, including Dr. Richard Davis and Mr. Matthew Aro, both from UMD. The PI is also willing to support the long-term implementation of this technology using his UMD startup funds.

## **Project Manager and Organization Qualifications**

**Project Manager Name:** Sam Toan

**Job Title:** Assistant Professor

**Provide description of the project manager’s qualifications to manage the proposed project.**Dr. Sam Toan, Principal Investigator (PI), is an Assistant Professor of Chemical Engineering at UMD. He has a strong background in materials chemistry, electrochemistry, chemical process, and catalysis studies, particularly in CO2 capture and conversion catalysis work. His work has been published in more than 30 high-quality journals, such as Nano Energy and Nature Communications. In addition, he developed several complex chemical process systems to capture CO2 from a variety contaminated sources. With his strong background in CO2 capture and conversion processes, the he has the experience to achieve excellent performance in the proposed project and has the capacity and resources to execute this research work at UM-Duluth.

**Organization:** U of MN - Duluth

**Organization Description:**The University of Minnesota Duluth (UMD) is a public, comprehensive regional university that is part of the University of Minnesota System. Offering 16 bachelor’s degrees in 87 majors and graduate programs in 24 fields, UMD faculty, staff, and students work together to produce high-quality research that benefits people in Minnesota and beyond. The main research areas targeted by UMD and its Natural Resources Research Institute (NRRI) include ecology and natural resource management, renewable energy, advanced materials and chemistry, minerals and metallurgy, and bioeconomy development. UMD and NRRI collaborate broadly across the University system, the state and the region to address the challenges of a natural resource-based economy. By partnering with industry, business leaders, agency decision-makers and many others, UMD and NRRI researchers frame and deliver on real-world solutions. In the proposed research, the team will access UMD’s chemistry and chemical engineering research expertise in CO2 capture and characterization, advanced analytical equipment in UMD’s Research Instrumentation Laboratory, and NRRI’s expertise and software for life cycle assessment (LCA) modeling.

## **Budget Summary**

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Category / Name** | **Subcategory or Type** | **Description** | **Purpose** | **Gen. Ineli gible** | **% Bene fits** | **# FTE** | **Class ified Staff?** | **$ Amount** |
| **Personnel** |  |  |  |  |  |  |  |  |
| Sam Toan |  | PI |  |  | 25% | 0.16 |  | $25,929 |
| Richard Davis |  | Co-PI |  |  | 25% | 0.16 |  | $42,206 |
| Matthew Aro |  | Co-PI |  |  | 25% | 0.24 |  | $24,587 |
| Postdoc |  | Postdoc |  |  | 17.3% | 2 |  | $143,203 |
| Graduate Student |  | Graduate Student |  |  | 19.1% | 0.5 |  | $28,512 |
| PhD Graduate Student |  | Graduate Student |  |  | 42.1% | 125 |  | $116,677 |
|  |  |  |  |  |  |  | **Sub Total** | **$381,114** |
| **Contracts and Services** |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  | **Sub Total** | **-** |
| **Equipment, Tools, and Supplies** |  |  |  |  |  |  |  |  |
|  | Tools and Supplies | Lab supplies and Chemicals | consumable lab supplies and chemicals will be used to operate the proposed project |  |  |  |  | $29,318 |
|  | Tools and Supplies | Life Cycle Analysis software fee | The license is needed to work on the LCA task |  |  |  |  | $2,568 |
|  |  |  |  |  |  |  | **Sub Total** | **$31,886** |
| **Capital Expenditures** |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  | **Sub Total** | **-** |
| **Acquisitions and Stewardship** |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  | **Sub Total** | **-** |
| **Travel In Minnesota** |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  | **Sub Total** | **-** |
| **Travel Outside Minnesota** |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  | **Sub Total** | **-** |
| **Printing and Publication** |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  | **Sub Total** | **-** |
| **Other Expenses** |  |  |  |  |  |  |  |  |
|  |  | Lab/Scientific Services | Material characterization fees |  |  |  |  | $8,000 |
|  |  |  |  |  |  |  | **Sub Total** | **$8,000** |
|  |  |  |  |  |  |  | **Grand Total** | **$421,000** |

### **Classified Staff or Generally Ineligible Expenses**

|  |  |  |  |
| --- | --- | --- | --- |
| **Category/Name** | **Subcategory or Type** | **Description** | **Justification Ineligible Expense or Classified Staff Request** |

### **Non ENRTF Funds**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Category** | **Specific Source** | **Use** | **Status** | **Amount** |
| **State** |  |  |  |  |
|  |  |  | **State Sub Total** | **-** |
| **Non-State** |  |  |  |  |
| In-Kind | University of Minnesota | Unrecovered indirect costs at 55% of MTDC project costs of $387,820. | Secured | $213,301 |
|  |  |  | **Non State Sub Total** | **$213,301** |
|  |  |  | **Funds Total** | **$213,301** |

## **Attachments**

### **Required Attachments**

#### ***Visual Component***

File: [6941ba7b-b47.pdf](https://lccmrprojectmgmt.leg.mn/media/map/6941ba7b-b47.pdf)

#### ***Alternate Text for Visual Component***

CO2 emissions from fossil fuel combustion power plants in Minnesota will be efficiently captured and converted to butanol to help Minnesota reach its greenhouse gas (GHG) emission targets and reduce GHG's negative impacts on the climate....

### **Optional Attachments**

#### ***Support Letter or Other***

|  |  |
| --- | --- |
| **Title** | **File** |
| Letter of Support from MN Power | [bd29e933-19e.pdf](https://lccmrprojectmgmt.leg.mn/media/attachments/bd29e933-19e.pdf) |
| LCCMR Transmittal letter Toan | [c374b9d8-48b.pdf](https://lccmrprojectmgmt.leg.mn/media/attachments/c374b9d8-48b.pdf) |

## **Administrative Use**

**Does your project include restoration or acquisition of land rights?**
 No

**Does your project have potential for royalties, copyrights, patents, or sale of products and assets?**
 Yes

**Do you understand and acknowledge IP and revenue-return and sharing requirements in 116P.10?**
 Yes

**Do you wish to request reinvestment of any revenues into your project instead of returning revenue to the ENRTF?**
 No

**Does your project include original, hypothesis-driven research?**
 Yes

**Does the organization have a fiscal agent for this project?**
 No