The growing demand for energy has a significant negative impact on the natural environment due to the emissions generated during the extraction, transportation, and use of fossil fuels. The level of $CO_2$ in the atmosphere is rising dramatically, more than ever in Earth's history, reaching 404 ppm in July 2017 and likely approaching 600 ppm by 2100 [1]. To counteract this trend, renewable energy sources such as solar and wind power, as well as sustainable resources like air and water, are essential to replace fossil fuels and reduce greenhouse gas emissions in the production of key chemicals and fuels. A promising solution is the direct capture of carbon dioxide ($CO_2$) from the atmosphere (or $CO_2$ directly from emission sources) and the use of renewable energy to power reactors for the electrochemical conversion of $CO_2$ ($eCO_2RR$) into valuable products essential for the chemical industry.

This project focuses on developing innovative catalysts aimed at enhancing the efficiency of this process. Catalysts required for this reaction must meet several critical process-related requirements, ensuring high performance under challenging operating conditions. These challenges include the accumulation of a carbon layer, known as coke, which can cover the active surface of the catalyst and reduce its effectiveness, as well as poisoning by sulfur compounds ($SO_2$), which can degrade the activity and durability of the catalyst. The project's goal is to develop new, durable catalysts resistant to coke formation and sulfur poisoning, capable of efficiently converting $CO_2$ into hydrocarbons over extended periods.

To achieve this goal, the project will be dedicated to the development of layered bimetallic catalysts (Ag, Zn, Al)-Cu and trimetallic catalysts (Pd, Mo)-(Ag, Zn, Al)-Cu for use in flow reactors, employing a technique called physical vapor deposition (PVD). PVD enables controlled deposition of metal layers such as copper (Cu), silver (Ag), zinc (Zn), aluminum (Al), palladium (Pd), and molybdenum (Mo) onto conductive carbon-based substrates (gas-diffusion electrodes). Copper-based (Cu) electrocatalysts are among the most promising candidates for $eCO_2RR$ due to their versatile ability to convert $CO_2$ into various products [2]. The PVD method ensures precise control over composition, layer thickness, and, in certain cases, metal distribution, allowing the creation of catalysts optimized for both high performance and long-term stability. The layered structure of these catalysts enables tailoring their properties, and the selected combination of metals aims to improve specific aspects of catalyst performance, such as selectivity and efficiency in producing various hydrocarbons, including methane and ethylene.

The project will begin with the fabrication of bimetallic catalysts consisting of (Ag, Zn, Al)-Cu layers, with precise control over parameters such as composition, deposition rate, and layer thickness. These catalysts will then undergo detailed physicochemical characterization to investigate their microstructure, surface morphology, and elemental distribution. This will help identify the relationships between catalyst structure and its electrocatalytic performance. The bimetallic catalysts will be tested under both standard conditions and environments containing $SO_2$ to evaluate their resistance to coke formation and sulfur poisoning, the two main factors limiting the durability of $eCO_2RR$ catalysts. Performance will be assessed over extended reaction periods to determine how the catalysts behave during long-term use. Various analytical techniques will be applied to monitor fresh and spent catalysts, providing insights into the mechanisms of their degradation. The results of the bimetallic catalyst analysis will serve as the foundation for the next stage: developing trimetallic catalysts containing additional palladium (Pd) and molybdenum (Mo) as promoters. These elements are expected to enhance resistance to coke deposition (Pd) and sulfur poisoning (Mo), which are crucial for maintaining the long-term activity of the catalysts. The research team will optimize the PVD process for these systems to ensure precise control over metal distribution, layer thickness, and catalyst structure. Detailed morphological studies will also be conducted to examine the roles of Pd and Mo in mitigating the effects of coke formation and sulfur poisoning, providing deeper insights into how these elements improve the overall stability of the catalysts.

The project will emphasize understanding the relationships between catalyst structure and composition, current efficiency, and process selectivity. By investigating both bimetallic and trimetallic catalysts, the project will provide new insights into factors affecting the electrochemical reduction of $CO_2$ under typical operating conditions. These findings will be crucial for designing more efficient, durable, and cost-effective catalysts for industrial applications, potentially making a significant impact on improving $CO_2$ conversion technologies and global efforts to combat climate change. This research will also deliver valuable insights into the design of flow systems for the electrochemical reduction of $CO_2$. The results of the project may represent an important step toward a sustainable future.

[1] Fan, Q. et al., *Materials Today Energy* 10 (2018) 280-301.
[2] Ma, L. et al., *Adv. Energy Sustainability Res.* 4 (2023) 2300034.