Summary

The chemical industry, along with cement and steel, is a major source of global industrial emissions. Several strategies can be implemented to pursue a deep **decarbonization of the industrial sector**; however, this remains a highly challenging task. Among these strategies are the deployment of alternative carbon feedstocks and energy sources (e.g., CO_2, biomass, electricity) and the capture and sequestration of carbon (CCS) at emission sources. Clean electricity is considered pivotal as the primary source of energy. Indeed, there is a huge interest in powering chemical processes with renewable electricity. One of the approaches to electrifying the chemical industry is manufacturing chemicals via the **electrochemical conversion of CO_2**, which will be introduced and explored throughout **Chapter 1**. This route offers several competitive advantages compared to conventional and thermochemical counterparts. The driving force behind electrochemical processes is electricity, which enables operations at ambient temperature and pressure, gives opportunities for cost savings in downstream separation, and mitigates the risks of thermal losses and catalyst sintering. Moreover, CO_2 electrolyzers can facilitate integration into existing infrastructure due to their modular design.

CO_2 molecules in the electrochemical system interact with both the electrolyte and the electrode. When a negative bias is applied to drive the CO_2 reduction, ions in the solution redistribute, and cations are attracted to the negatively charged surface of the electrode. The ion-based layer, known as the electric double-layer (EDL), governs the local environment and influences the movement of molecules as well as the stability of reaction intermediates. **Different electrolytes and electrodes** give rise to EDLs with distinct properties, which, in turn, direct **different activity and selectivity** of the processes.

Nearly all research in this field has been conducted using pure CO_2. However, a potential approach to improving the efficiency and sustainability of the electrochemical conversion of CO_2 is to integrate this process with CO_2 capture systems. An alternative approach to further reduce costs is to **bypass the capture step entirely by directly feeding the fluid containing CO_2** into the cell for conversion. However, in addition to **other reactive components such as oxygen or nitrogen oxides**, CO_2 reduction processes involving flue gas are significantly affected by the reduced concentration of CO_2, which impacts the **mass transport**.

The setup of the electrolyzer significantly influences the efficiency of the process. It affects several aspects, such as the rate at which the feed gas is transferred to the catalyst, the cell resistance, and the management of liquid products across the electrodes. An **efficient design for a liquid-fed device is the three-chamber cell that features a gas diffusion electrode (GDE)**, whose primary advantage lies in its porosity, which allows direct delivery of the reactant to the active sites and results in higher diffusion coefficients and mass transfer

rates – overcoming the issues commonly reported in batch cells. Typically, an **ion exchange membrane** is employed in a flow cell system. It performs several key functions, including **maintaining the desired local conditions** and ensuring **proper ionic conductivity**, thereby contributing effectively to reaction selectivity.

The primary objective of this thesis is to address key challenges associated with the electrochemical conversion of CO_2 on gas diffusion electrodes, aiming to advance the field and help bridge the gap to industrial implementation. In this context, **Chapter 2** of this dissertation will present and discuss the results obtained on a Cu_2O/SnO_2-based catalyst in the presence of a 1-butyl-3-methylimidazolium triflate ([BMIM][TfO]) in acetonitrile electrolyte. Here, organic electrolytes have been studied to evaluate the co-catalytic properties of ionic liquids in continuous flow cells, thus far only been demonstrated in batch reactors. **Chapter 3** will present and discuss the activity and selectivity of the Cu_2O/SnO_2-based GDE in the presence of a flowing aqueous electrolyte. Here, to advance the industrial application of such systems, the effect of simulated flue gas has been studied and discussed, with a specific focus on CO_2 dilution and O_2 as an impurity. Maintaining selectivity as the cell area increases remains one of the most challenging tasks. **Chapter 4** will illustrate the hurdles that have been encountered during the transition from a commercial 10 cm^2 scale to a customized 100 cm^2 cell, which represents one of the 20 repeating units of the SunCoChem prototype. Operations in the presence of aqueous electrolytes have been coupled with in-operando electrochemical impedance spectroscopy for the early identification of failure modes.

Carbon monoxide (CO) is one of the most promising products via the electrochemical route. Companies and startups have demonstrated operations at industrially relevant currents and extended lifetimes; however, pilot and demo projects are necessary to assess investment costs and maintenance expenses. **Chapter 5** will present the development of a stable GDE and the systematic evaluation of various factors influencing CO_2 conversion on a well-established Ag catalyst, with the ultimate goal of advancing this technology toward real-world applications.

The cascade concept, where CO_2 is first converted into CO and then CO is strategically converted into target molecules, is gaining increasing attention. **Chapter 6** will present the results of the investigation into selectivity variations arising from CO_2 and CO reduction on bimetallic CuZn systems. These results were obtained during a research period at the Helmholtz Zentrum Berlin.

Finally, **Chapter 7** will summarize the conclusions of each chapter (from 2 to 6) and critically analyse the results obtained, highlighting potential future developments and areas for improvement. This thesis work was carried out within the framework of the European Union-funded SunCoChem project.