Alkene epoxidation is a crucial chemical functionalization reaction that produces key chemical intermediates for the synthesis of various commercial end products. The current methods of producing epoxides are associated with a number of challenges, including the use of energy-intensive and hazardous oxidants such as chlorine or peroxides. An alternative process using molecular oxygen as a reagent is available, but it requires elevated temperatures and pressures, which pose significant safety concerns. To improve the safety and efficiency of epoxide production, there is a need for new methods that can overcome these limitations and enable the production of epoxides in a more sustainable and safe manner. From this perspective, this thesis work explores electrochemical alkene epoxidation using water as the oxygen source, delving into both fundamental and practical aspects of chlorine-mediated and direct approaches.

We first discuss the mechanism of chlorine-mediated ethylene oxidation in saline water. Chlorine can be a promising species as a redox mediator since natural saline water provides an abundant source of chlorides. We demonstrated that electrochemically generated chlorine selectively oxidizes ethylene to chloroethanol, which converts to ethylene oxide in alkaline aqueous electrolytes. Through electrochemical kinetic studies, we reveal that the chlorine-mediated ethylene oxidation mechanism changes in the presence and absence of ethylene; integrating ethylene oxidation with chlorine evolution in a single reactor makes the electrochemical chlorine evolution less efficient.

We then shift focus to direct alkene epoxidation, investigating the influence of single-atom dopants on manganese oxide in relation to the electrochemical direct epoxidation. Manganese leaching during galvanic replacement introduces lattice vacancies that make the nanoparticles more susceptible to metal oxidation and catalyst reconstruction under an applied anodic potential. Highly electrophilic oxygens induced by adjacent electron-poor metals were implicated in the observed enhancement in electrocatalytic cyclooctene epoxidation.

Lastly, we present a sustainable and selective method for propylene epoxidation using an oxidized palladium-platinum alloy catalyst. This catalyst demonstrates remarkable Faradaic efficiency and rate toward epoxidation under ambient temperature and pressures, outperforming previously reported electrocatalysts for direct epoxidation. The reaction mechanism is investigated using a multi-faceted approach, including kinetic rate measurements, probe substrate analysis, and substrate-based descriptor assessment. This work advances sustainable epoxide synthesis, which currently has significant energy and environmental footprint.

This thesis work unveils the opportunities and challenges in electrochemical alkene epoxidation using water as the oxygen source, thereby establishing a solid foundation for future research endeavors. Significant advancements in catalyst development for direct electrochemical alkene epoxidation position this electrochemical approach as an appealing alternative to existing epoxide synthesis routes.