Influence of the electrode-electrolyte interface on electrochemical CO2 reduction reaction and hydrogen evolution reaction

Ye, C.

Summary and Outlook

Summary

Electrochemistry is a branch of chemistry focused on the interaction between electrical energy and chemical changes, playing a vital role in modern energy storage and conversion technologies. Since the early 21st century, it has gained substantial attention due to the growing concerns over climate change and the urgent need to transition away from fossil fuels. The increasing availability of low-cost electricity from renewable energy sources, such as solar and wind, has further underscored the need for efficient systems that can store and convert electrical energy into chemical bonds.

Over the past few decades, the electrochemical CO_2 reduction reaction (CO_2RR) has been extensively studied for its potential to convert CO_2, a major contributor to global warming, into valuable chemicals and fuels like formic acid, carbon monoxide, and hydrocarbons, using renewable energy. This process presents a promising solution for mitigating industrial CO_2 emissions while contributing to the global shift toward green energy and carbon neutrality. However, despite significant achievements made so far, CO_2RR still faces significant challenges, including low activity and selectivity, catalyst degradation, and low overall energy efficiency, all of which limit its scalability for industrial applications.

This thesis will focus on these challenges and explores strategies to optimize CO_2RR performance from different aspects. The first part (Chapter 2) investigates the influence of organic additives on CO_2RR activity and selectivity, as well as their effects on the interfacial environment during CO_2RR. The focus then shifts to a well-defined surface in Chapter 3, where we closely examine the role of metal cations on CO_2RR using a palladium monolayer modified Pt(111) surface ($Pd_{ML}Pt(111)$) in a pH 3 electrolyte. In Chapter 4, we further investigate the influence of metal cations on the competing hydrogen evolution reaction (HER) in mildly acidic media, which is relevant for optimizing CO_2RR performance. Finally, in chapter 5, we expand the scope to industrially relevant conditions by studying the

influence of bulk electrolyte pH on CO_2RR product distribution using a copper gas diffusion electrode (Cu GDE).

The thesis starts in chapter 2 with a study on CO_2RR using poly(4-vinylpyridine) (P4VP) modified copper (Cu) and gold (Au) electrodes. We show that modifying Cu and Au electrodes with P4VP enhances formic acid formation during CO_2RR, especially at low overpotentials. With in situ ATR-SEIRAS and contact angle measurements, we attribute the improved selectivity towards formic acid to the hydrophobic nature of the P4VP layer, which limits the transport of proton donors, i.e. bicarbonate (HCO_3^-) and water, from the bulk electrolyte to the reaction interface, effectively suppressing HER.

Chapter 3 investigates the influence of cations on formic acid and CO formation during CO_2RR using a palladium monolayer modified platinum ($Pd_{ML}Pt(111)$) electrode. We observe that the onset potentials for formic acid and CO formation shift positively with increasing cations concentration, with a pronounced effect on formic acid formation. Theoretical simulations suggest that cations facilitate both hydride formation and CO_2 activation by polarizing the electronic density at the surface and stabilizing $*CO_2^-$. In addition, the simulations indicate that high CO coverage inhibits hydride formation, leading to a rapid decrease of formic acid selectivity at higher applied potentials.

In Chapter 4, we study the role of metal cations in the HER on a polycrystalline platinum electrode in mildly acidic media. We show that increasing cation concentration significantly enhances water reduction but does not kinetically influence proton reduction at lower potentials. In addition, we identify a non-negligible migration current under mass transport limited conditions in electrolytes with low cation concentration, highlighting the importance of sufficient supporting electrolyte in minimizing this migration current. We further show that, adding strongly hydrated cations, e.g. Li^+, to a K^+ containing electrolyte, shifts the onset potential for water reduction positively, suggesting that strongly hydrated cations (Li^+) promote water dissociation more effectively compared to weakly hydrated cations (K^+).

In Chapter 5, we investigate the effect of bulk electrolyte pH on CO_2RR product distribution using Cu GDE. We show an inhibited hydrogen formation at low current densities in a mildly acidic electrolyte compared with a traditional bicarbonate electrolyte, and similar CO_2RR product distributions in both electrolytes at higher current densities. Additionally, we highlight that, despite the promising prospects of acidic media for CO_2RR, electrode degradation remains a challenge for long-term electrolysis, particularly in acidic bulk electrolytes.

Outlook

The future of electrochemical CO_2 reduction lies in overcoming key challenges such as improving selectivity, enhancing catalyst stability, and ensuring scalability for industrial applications. Significant progress has been made in catalyst design, particularly through nanostructuring and the use of organic additives, which have shown potential in improving reaction efficiency. In addition, optimizing the electrolyte composition and engineering the reaction environment at the electrode-electrolyte interface are critical to improving CO_2RR performance. The development of more robust electrolyzer systems, such as GDE systems, is another essential aspect for practical implementation of CO_2RR technologies. Despite the considerable achievements thus far, continued research into reaction mechanisms and electrode-electrolyte engineering as well as electrolyzer system engineering will be necessary to unlock the full potential of CO_2RR in industrial applications.