Unveiling the electrolyte effects of CO2 electroreduction to CO and H2 evolution from the interfacial pH perspective

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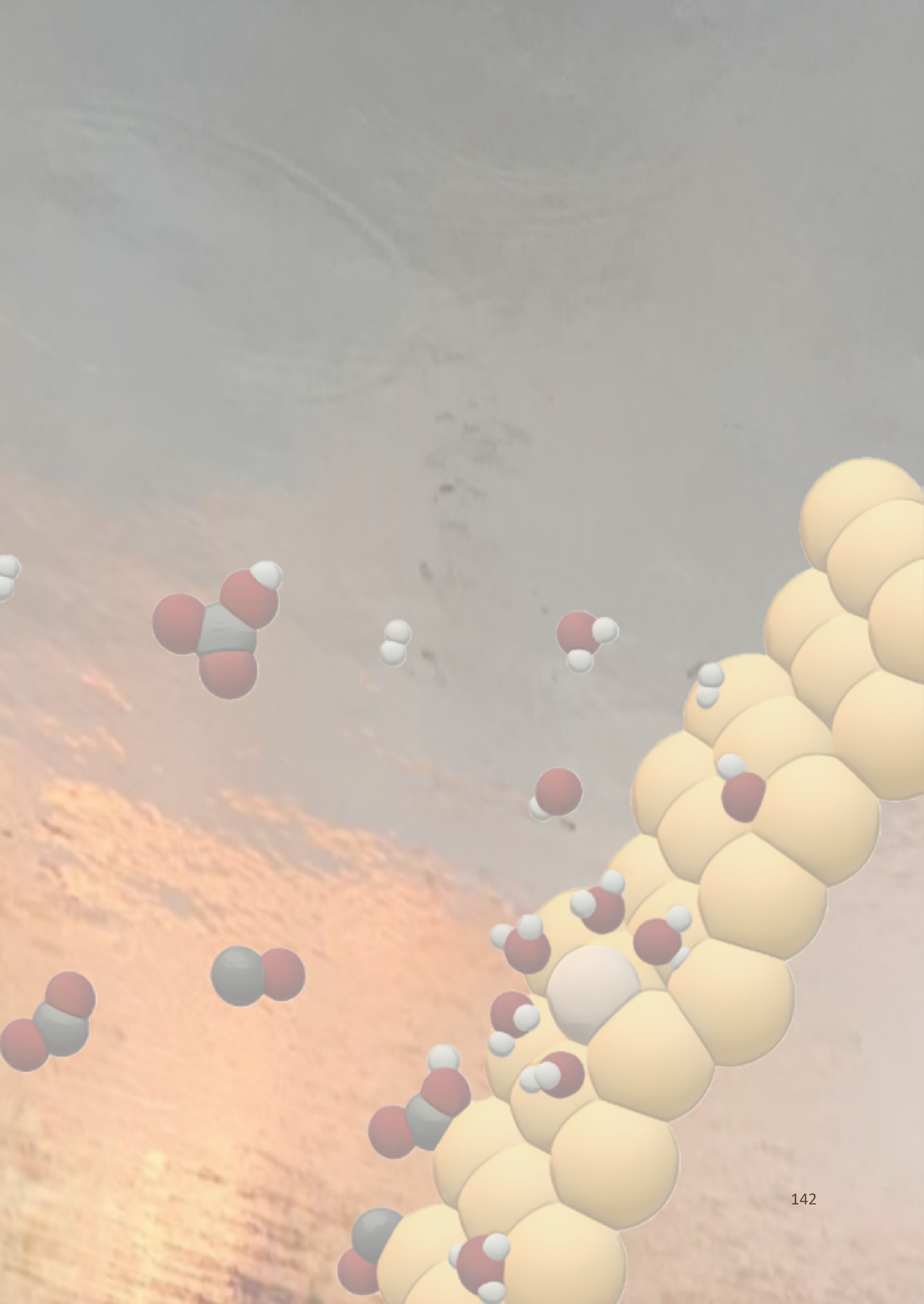

Summary

The role of the interfacial environment during electrochemical reactions has been increasingly valued, especially for those reactions involving protons or hydroxyl ions. The acid-base equilibria of the weak proton donors in the bulk electrolyte, namely the protic anions and the weakly hydrated cations, implicitly modify the interfacial environment and impact the rate and selectivity of electrochemical reactions. Therefore, the interfacial pH is key to unveil the electrolyte effects. In this thesis, we devised an in-situ interfacial pH sensor and visualized the evolution of interfacial pH during the electroreduction of CO_2 to CO and H_2 evolution. We found that the reaction activity and competition between CO_2 electroreduction to CO and H_2 evolution is highly dependent on interfacial pH, which can be readily tuned by modulating the interfacial environment *via* various electrolyte species.

Coupled with the highly sensitive voltammetric 4-hydroxylaminothiophenol/4-nitrosothiophenol (4-HATP/4-NSTP) pH sensing redox couple, the Au ring of the RRDE can be used as a robust in-situ pH meter under well-defined mass transport conditions. In **Chapter 2**, the RRDE pH sensor is proved to be capable of recording the interfacial pH during electrode reactions on the Au disk over a wide pH range, without imposing further interference to the reactions. We showed that the interfacial pH during the H_2 evolution was influenced by the potential, or more precisely the current density drawn, the rotation rate, and the buffer capacity. The RRDE setup quantifies how a more negative potential and a larger current density lead to the increase of interfacial pH, while a higher rotation rate and a larger buffer capability suppress it.

As for the CO_2 reduction, the situation is different due to the buffering of CO_2 and HCO_3^-. **Chapter 3** demonstrated that two pH regimes appear with increasing polarization during CO_2 reduction. The interfacial pH stabilizes at around 7 due to the buffering of CO_2 at a less negative potential and jumps to 9 as the interfacial CO_2 concentration decays and HCO_3^- starts to buffer. This also leads to the decay of CO_2 electroreduction and the enhancement of the competing water reduction. The interfacial environment is modified by changes in mass transport and buffer capacity. Also the size and concentration of the cation can suppress the rise in the interfacial pH. The results showed that the anion buffer has the largest effect, while the mass transport and the cations are not as efficient in resisting interfacial pH changes. In fact, increasing mass transport by changing the disk rotation rate appears to be the least effective, as the interfacial pH is still as high as 11 under strong forced convection (2500 rpm). Importantly, increasing buffer or cation concentration might not assist in CO_2 electroreduction, since the competing HER is typically more enhanced by that than the CO_2 electroreduction.

To maintain the interfacial CO_2 concentration, in **Chapter 4**, the CO_2 electroreduction was conducted under mildly acidic electrolyte conditions (at pH 3). We proved that the CO_2 electroreduction outcompetes the proton reduction and increases along the proton mass transport-limited current plateau under a near-neutral interfacial environment, which is attributed to the consumption of the protons by the hydroxyl ion generated by the CO_2 electroreduction. However, when the water reduction regime sets in, the local alkaline environment leads to extra consumption of CO_2 by the hydroxyl ion. Besides, the reaction selectivity towards CO_2 electroreduction can be further improved by tuning the interfacial environment *via* the anion effect, cation effect, and mass transport effect. A proper protic anion such as HSO_4^- can add extra proton flux *via* the acid-base equilibra to maintain the environment to be nearly neutral. In an acidic environment, a weakly hydrated cation such as K^+ accelerates the CO2RR while barely impacting the competing proton reduction, whereas decreasing the mass transport suppresses the proton reduction, leading to a higher selectivity of the CO2RR.

The investigation of the effects of these supporting electrolyte species on H_2 evolution was continued in **Chapter 5**. We observed that the steady-state current of H_2 evolution appreciably increases with the concentration of the protic anion, namely HSO_4^- and the weakly hydrated alkali cations (K^+ and Cs^+). This enhancement is attributed to the coupling of proton reduction with the homogeneous acid-base equilibria, namely, the dissociation of HSO_4^- and hydrolysis of K^+ and Cs^+. This confirmed the buffering capability of the alkali cation species and their implicit role as a weak proton donor, which can be observed and quantified experimentally using RDE. Quantitative studies elucidated the H_2 evolution in this case as a mass transport limited process coupled to a chemical reaction (i.e. the acid-base reaction). Moreover, the linear relationship between the concentration of electro-inactive species and the Koutecký-Levich slope was observed, from which the pK_a of the proton donor involved can be extracted. The corresponding pK_a 's of HSO_4^-, K^+, and Cs^+ were determined to be 2.06, 2.52, and 2.48, respectively.