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Role of near-surface environment in tuning electrochemical CO₂ reduction reaction and H₂ evolution reaction

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Summary

This thesis has shed light on some of the ways in which the local electrolyte composition can differ from the bulk and how these changes in the local reaction environment can determine the activity and/or selectivity of two electrocatalytic reactions, namely, electrochemical CO₂ reduction reaction (CO₂RR) and hydrogen evolution reaction (HER).

In **chapter 2** of this thesis we adapted the well-known rotating ring disk electrode (RRDE) technique to study the role of mass transport in tuning the competition between CO₂RR and HER on Au catalysts. The idea was to systematically tune the local concentration gradients at the catalyst surface by the means of hydrodynamic convection control and to quantify the formed amounts of CO and H₂ during the reactions in an online fashion. This was important to avoid any convolutions due to time-based concentration polarization effects. We found that the rate of CO₂RR increased slightly with the increasing rotation rate (i.e. mass transport) of the electrode. We attributed this enhancement to the suppression of local consumption of CO₂ via its homogeneous acid-base equilibria. Interestingly, in contrast with CO₂RR, the increasing rotation rate of the electrode led to the suppression of the competing HER reaction (in 0.1 M bicarbonate containing electrolytes). We showed that this suppression stems from the pH dependence of HER, since on Au catalysts, the HER activity increases with increasing pH of the electrolyte. Thus, with increasing rotation rate of the electrode, as the locally generated hydroxyl ions are transported away from the electrode surface, and the HER activity decreases. As a result, the Faradaic selectivity for CO₂RR enhances significantly with increasing rotation rate of the electrode, in part due to the slight enhancement of CO formation rate but mostly due to the suppression of competing HER reaction.

In **chapter 3** we further investigated the pH dependence of HER in alkaline media on Au catalysts. We found that the pH dependence of HER is in-fact inter-linked with the cation concentration dependence of this reaction. We showed that the cations near the surface enhance the rate of HER by stabilizing the transition state for the rate determining Volmer step (water dissociation step) of this reaction. Interestingly, since the changing electrolyte pH leads to changes in the interfacial electric field, this in-turn results in changing near-surface cation concentration. In particular, with increasing electrolyte pH, the interfacial electric field becomes more negative and this results in a corresponding increase in the local concentration of cations. Hence, the enhancement in HER activity with increasing electrolyte pH is in-fact due to the increase in the near-surface cation concentration. Moreover, we showed that if we keep increasing the near-surface cation concentration, either by increasing the bulk cation concentration or by increasing the electrolyte pH, at some point the promotional effect of cations on HER saturates and even becomes inhibitive. This shows that beyond a threshold concentration, the cations near the surface can lead to blocking of the active sites for HER, either due to direct adsorption at the catalyst surface or due to the crowding of the double layer.

In **Chapter 4** of this thesis, we reconciled the findings of Chapter 2 and Chapter 3 by further investigating the rotation rate dependence as well as the cation identity dependence of HER on Au electrodes. We pointed out in this work that though the bulk pH and the local pH affect the HER activity by tuning the near-surface cation concentration, they do it in two distinct ways. In the case of bulk pH changes, near-surface cation concentration responds to the changes in the interfacial electric field strength (as described in Chapter 3). However, local pH changes (via rotation rate control) tune the local cation concentration, simply because of the need to satisfy local electroneutrality. Moreover, we also show in this work that depending on the hydration energy of cations, the strength of the cation-metal interactions can be tuned, which can also result in varying HER activity trends.

Lastly, in **Chapter 5** we implemented the understanding gained in the previous chapters to study the role of pore parameters (diameter and length) in tuning the local reaction environment and hence the activity/selectivity of CO₂RR and HER on nanoporous Au catalysts. To do so, we employed our home-built differential electrochemical mass spectrometry (DEMS) technique which allows for the online, quantitative detection of CO and H₂ over the course of CO₂RR and HER. We found that similar to the flat Au catalysts (Chapter 2), the changes in the local concentration gradients in nanoporous catalysts mainly affect the HER activity. Notably, we could show that due to the presence of additional ohmic drop effects in the nanoporous channels, the entirety of the nanoporous catalysts do not actually participate in electrocatalysis and these ohmic drop effects scale with the length of the pores.