Electrocatalytic reduction of CO2 and nitrate on immobilized metal porphyrins

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Summary

This thesis discusses the parameters affecting the catalysis for the electrochemical reduction of small molecules, such as carbon dioxide and nitrate, on immobilized metal-porphyrin catalysts. The relatively high overpotentials and the competing hydrogen evolution reaction (HER) are the major bottlenecks in the electrochemical reduction of these two molecules, which reduces their efficiency for the reduction to useful chemicals.

Carbon dioxide is an abundant greenhouse gas in the atmosphere. It would be ideal if we could convert carbon dioxide into valuable chemicals, such as carbon monoxide, methanol, methane and ethylene, by using renewable energy, such as sun light and wind. The electrochemical reduction of carbon dioxide is a promising approach to achieve this goal. Different kinds of catalysts have been studied for the electrochemical reduction of carbon dioxide. Metal electrodes have been divided into different groups based on the products they produce from carbon dioxide reduction. Most metal electrodes form 2-electron transfer products, such as carbon monoxide, formic acid and oxalic acid. Copper is an exceptional electrode, which is able to reduce carbon dioxide to methane and ethylene. Except metal electrodes, metal complexes are also effective catalysts. However, in spite of the extensive investigations, the mechanism of the carbon dioxide reduction is still unclear. The research presented in this thesis is focused on the parameters that influence the carbon dioxide reduction as well as on the insights into the mechanism on metal porphyrin electrode.

Nitrate is commonly used as fertilizer in agriculture and as an explosive. However, the abusive use of nitrate can cause its accumulation into ground water, which is harmful for human health. High concentration of nitrate in drinking water, 10 mg/L, can lead to blue baby syndrome. Previous work from our laboratory has offered detailed studies on the electrochemical reduction of nitric oxide and nitrite on immobilized iron porphyrin. Hydroxylamine was found to be the main product. pH plays an important role in both the

nitric oxide and nitrite reduction. The studies in this thesis are focused on the mechanism of and pH influence on the electrochemical reduction of nitrate on the metal porphyrin catalyst.

The thesis starts in chapter 2 with a study of the electrochemical reduction of carbon dioxide on a cobalt protoporphyrin (PP) modified pyrolytic graphite electrode in aqueous solution. We study the reduction of possible intermediates of the carbon dioxide reduction, such as carbon monoxide, formic acid and formaldehyde, and the influence of pH on the carbon dioxide reduction and the hydrogen evolution reaction. Based on our investigations, we propose a possible mechanism in which a CO_2^- anion initially binds to the complex $[Co(PP)\text{-}(CO_2)]^-$ by an electron transfer. The CO_2 anion acts as an Brønsted base to abstract a proton from water molecule to form a "carboxyhydroxyl" intermediate [Co(PP)-(COOH)]. The [Co(PP)-(CO)] complex is subsequently formed from a [Co(PP)-(COOH)] intermediate, which leads either to the formation of CO or to the further reduction to CH_4 through a series of concerted proton-electron transfer steps.

In chapter 3, we perform a theoretical study using density functional theory (DFT) on the electrochemical reduction of carbon dioxide on a cobalt porphyrin (P) catalyst. Cobalt porphyrin, $[Co^{II}P]$, is reduced to $[Co^{I}P]^-$ to act as the active state for the formation of the $[Co(P)\text{-}(CO_2)]^-$ anion adduct, which is consistent with our experimental observations in Chapter 2. The formation of [Co(P)-(COOH)] intermediate is competing with that of [Co(P)-(OCHO)] intermediate. Our calculations and experiments suggest that the formation of [Co(P)-(COOH)] probably goes through decoupled proton-electron transfer steps, while the formation of [Co(P)-(OCHO)] is through concerted proton-electron transfer steps. This observation can explain the pH dependence of the reduction of carbon dioxide. The formation of methanol as an intermediate is also inferred from our calculations. The electrochemical reduction of methanol on the immobilized cobalt protoporphyrin shows that methanol is indeed reduced to methane.

Various metal protophophyrins are utilized as catalysts for the electrochemical reduction of nitrate in Chapter 4. Among the different metal-centered protophophyrins, cobalt protophophyrin shows the highest selectivity toward hydroxylamine, which makes it

the most interesting catalyst. Besides hydroxylamine, a smaller amounts of ammonia and N_2O are found. The activity for the nitrate reduction is highly affected by pH, because the rate-determining step, the nitrate reduction to nitrite, is highly sensitive to the pH. Interestingly, also the selectivity for hydroxylamine vs. ammonia is very pH sensitive. Two possible mechanisms, a sequential pathway and parallel pathway for the formation of hydroxylamine and ammonia, have been proposed, with the sequential pathway being the most consistent with the observed pH sensitive selectivity.

In summary, this thesis has shown that the metal porphyrin complexes are effective catalysts for both the electrochemical reduction of carbon dioxide and nitrate. The insights into the mechanism for both reactions offer the opportunity for the design of new effective catalysts in the future.