Electrocatalytic reduction of CO2 and nitrate on immobilized metal porphyrins

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Propositions

accompanying the thesis

Electrocatalytic reduction of CO_2 and nitrate on immobilized metal porphyrins

1. Lack of insight into the mechanism of the carbon dioxide (CO_2) reduction offers the opportunity to make a significant influence.

2. The key intermediate in the pathway of CO_2 to carbon monoxide (CO) is CO_2 anion adduct onto reduced metal complex (Co^IP), while the further reduction of CO to methane goes through formaldehyde as an intermediate.

   Chapter 2 of this thesis

3. The CO_2^- anion adduct is formed through a decoupled proton-electron transfer process while the cobalt center of the complex is at Co^I oxidation state.

   Chapter 3 of this thesis

4. M-COOH is the key intermediate for the CO_2 reduction and competes with M-H which leads to the formation of hydrogen.

   Tripkovic, V.; Vanin, M.; Karamad, M.; Björketun, M. E.; Jacobsen, K. W.; Thygesen, K. S.; Rossmeisl, J., J. Phys. Chem. C 2013, 117, 9187-9195.

5. The $[Co^I(P)\text{-}(CO_2)]^{2-}$ intermediate obtains a proton from a neighboring H_3O^+ or H_2O to give $[CoP^{II}COOH]^-$ as next intermediate.

   Leung, K.; Nielsen, I. M. B.; Sai, N.; Medforth, C.; Shelnutt, J. A., J. Phys. Chem. A, 2010, 114, 10174-10184.

6. pH plays an important role at almost each step of the nitrate electroreduction on cobalt protoporphyrin immobilized pyrolytic graphite electrode. The formation of hydroxylamine and ammonia could go through either a sequential or a parallel pathway.

   Chapter 4 of this thesis

7. Sharp tools make good work. ---工欲善其事，必先利其器

   Kong Zi, The Analects

8. Our destiny offers not the cup of despair, but the chalice of opportunity. So let us seizeit, not in fear, but in gladness.

   R.M. Nixon

Jing Shen

Leiden, December 9, 2015