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## Electrocatalytic reduction of CO<sub>2</sub> and nitrate on immobilized metal porphyrins

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## Propositions

accompanying the thesis

### Electrocatalytic reduction of CO<sub>2</sub> and nitrate on immobilized metal porphyrins

1. Lack of insight into the mechanism of the carbon dioxide (CO<sub>2</sub>) reduction offers the opportunity to make a significant influence.
2. The key intermediate in the pathway of CO<sub>2</sub> to carbon monoxide (CO) is CO<sub>2</sub> anion adduct onto reduced metal complex (Co<sup>I</sup>P), while the further reduction of CO to methane goes through formaldehyde as an intermediate.

*Chapter 2 of this thesis*

3. The CO<sub>2</sub><sup>-</sup> anion adduct is formed through a decoupled proton-electron transfer process while the cobalt center of the complex is at Co<sup>I</sup> oxidation state.

*Chapter 3 of this thesis*

4. M-COOH is the key intermediate for the CO<sub>2</sub> 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<sup>I</sup>(P)-(CO<sub>2</sub>)]<sup>2-</sup> intermediate obtains a proton from a neighboring H<sub>3</sub>O<sup>+</sup> or H<sub>2</sub>O to give [Co<sup>II</sup>COOH]<sup>-</sup> 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 seize it, not in fear, but in gladness.

R.M. Nixon

Jing Shen

Leiden, December 9, 2015