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Iron complexes as electrocatalysts for the water oxidation reaction

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Citation

Kottrup, K. G. (2018, February 28). *Iron complexes as electrocatalysts for the water oxidation reaction*. Retrieved from <https://hdl.handle.net/1887/61046>

Version: Not Applicable (or Unknown)

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Title: Iron complexes as electrocatalysts for the water oxidation reaction

Date: 2018-02-28

Propositions (Stellingen)

accompanying the thesis

“Iron complexes as electrocatalysts for the water oxidation reaction”

1. Contrary to popular belief, chemical oxidants are not suitable for studying water oxidation catalysts under meaningful conditions.
This thesis, chapters 1 and 4
2. Changing the electrode material can have a profound influence on the outcome of electrochemical measurements.
This thesis, chapter 3
3. “True” outer sphere electron transfer between the working electrode and the catalyst is not as common one might think.
This thesis, chapters 3, 4 and 5
4. The ideal setup to study a water oxidation catalyst consists of three key parts: i) an inert, halide-free electrolyte salt that does not contain oxygen atoms, ii) a water-soluble, weakly coordinating pH buffer and iii) a redox inert and catalytically inactive electrode. Unfortunately all three parts remain elusive.
This thesis, chapter 2
5. Before a catalyst can be claimed to be homogeneous, adequate control experiments must be performed to rule out the *in situ* formation of catalytically active heterogeneous materials.
Z.-Q. Wang et al. *Appl. Catal., A* **2015**, 490, 128-132.
6. One cannot support the claim that a voltammogram is in agreement with previous reports by citing a reference which shows a fundamentally different-looking voltammogram.
Z. Borkowska; A. Tymosiak-Zielinska; G. Shul, *Electrochim. Acta* **2004**, 49, 1209-1220.

7. Before attempting to demonstrate that a dimeric complex does not dissociate over time one should first establish that the complex is dimeric to begin with.
L. D. Wickramasinghe et al., *J. Am. Chem. Soc.* **2015**, *137*, 13260-13263.
8. A catalyst with a turnover frequency of 0.15 s^{-1} should give more than 29 turnovers over the course of 15 h.
M. K. Coggins et al. *J. Am. Chem. Soc.* **2014**, *136*, 5531-5534.
9. Authors and reviewers of scientific literature need to apply just as much scrutiny to supporting information and experimental details as they do to results and discussion. Incomplete or erroneous procedures make it difficult to independently reproduce results which is not only frustrating but undermines scientific integrity.
M. Okamura et al. *Nature* **2016**, *530*, 465-468; W. S. Szulbinski; D. H. Busch, *Inorg. Chim. Acta* **1995**, *234*, 143-148; J. Yin et al. *J. Org. Chem.* **2007**, *72*, 4554-4557 ... and many, many more.
10. The availability of crucial lab equipment tends to be inversely proportional to the importance of the measurement one wishes to perform.
11. It is entirely possible to get very useful data out of a machine of which no one knows exactly how it works.
12. One of the biggest problems of the scientific community is a lack of appreciation for negative results.

Konstantin Kottrup
Leiden, December 2017