



Universiteit
Leiden
The Netherlands

Electroreduction of nitrate and carbon dioxide on copper electrodes: a mechanistic study

Perez Gallent, E.

Citation

Perez Gallent, E. (2018, February 1). *Electroreduction of nitrate and carbon dioxide on copper electrodes: a mechanistic study*. Retrieved from <https://hdl.handle.net/1887/61142>

Version: Not Applicable (or Unknown)

License: [Licence agreement concerning inclusion of doctoral thesis in the Institutional Repository of the University of Leiden](#)

Downloaded from: <https://hdl.handle.net/1887/61142>

Note: To cite this publication please use the final published version (if applicable).

Cover Page



Universiteit Leiden



The following handle holds various files of this Leiden University dissertation:

<http://hdl.handle.net/1887/61142>

Author: Perez Gallant, E.

Title: Electroreduction of nitrate and carbon dioxide on copper electrodes: a mechanistic study

Issue Date: 2018-02-01

ELECTROREDUCTION OF NITRATE AND CARBON DIOXIDE ON COPPER ELECTRODES

A mechanistic study

Proefschrift

ter verkrijging van

de graad van Doctor aan de Universiteit Leiden,

op gezag van Rector Magnificus Prof. Mr. C. J. J. M. Stolker

volgens besluit van het College voor Promoties

te verdedigen op donderdag 1 februari 2018

klokke 11:15 uur

door

Elena Pérez Gallent

geboren te Valencia, Spanje in 1988

Promotiecommissie

Promotor : Prof. Dr. M. T. M. Koper

Co-promotor : Dr. F. Calle-Vallejo

Overige leden : Prof. Dr. H. S. Overkleeft (Universiteit Leiden)

Prof. Dr. E. Bouwman (Universiteit Leiden)

Prof. Dr. Ir. B.M. Weckhuysen (Universiteit Utrecht)

Dr. W.A. Smith (Technische Universiteit Delft)

Dr. B.S. Yeo (National University of Singapore)

ISBN 978-94-6299-842-1

Printed by Ridderprint BV

Cover designed by Elena Pérez Gallent and Marta Ramirez Angulo

Life is and will ever remain an equation incapable of solution, but it contains certain known factors.

Nikola Tesla

Contents

1. Introduction	9
1.1 The Birth of Electrochemistry	10
1.2 Electrocatalysis.....	11
1.3 The potential of electrochemistry in industrial processes.....	12
1.4 Electrocatalytic reduction of nitrate.....	15
1.5 Electrocatalytic reduction of CO ₂	18
1.5.1 Electroreduction of CO ₂ to hydrocarbons.....	19
1.5.2 Electroreduction of CO ₂ to cyclic carbonates	22
1.6 Copper, an extraordinary catalyst	23
1.7 Scope and outline of this thesis.....	25
2. Electroreduction of nitrate on copper single crystals in acidic and alkaline media	29
2.1 Introduction.....	30
2.2 Experimental	31
2.3 Results and Discussion	34
2.3.1 Nitrate reduction in alkaline media.....	34
2.3.2 Nitrate reduction in acidic media	43
2.3 General discussion	48
2.4 Conclusions	49

3. Structure-sensitive electroreduction of acetaldehyde to ethanol on copper and its mechanistic implications for CO and CO₂ reduction.....	51
3.1 Introduction.....	52
3.2 Experimental.....	53
3.3 Computational details.....	54
3.4 Results and discussion.....	57
3.5 Mechanistic implications.....	61
3.5 Conclusions.....	64
4. Spectroscopic Observation of a Hydrogenated CO Dimer Intermediate During CO Reduction on Cu(100) Electrodes.....	65
4.1 Introduction.....	66
4.2 Experimental.....	67
4.3 Results and discussion.....	68
4.4 Conclusion.....	75
5. Structure and potential dependent cation effects on CO reduction at copper single crystal electrodes.....	77
5.1 Introduction.....	78
5.2 Experimental.....	80
5.3 Results and discussion.....	84
5.3.1 OLEMS and HPLC.....	84
5.3.2 FTIR.....	89
5.3.3 DFT calculations.....	92
5.3.4 Mechanistic implications.....	95
5.4 Conclusions.....	99

6. Mechanistic study of the electrosynthesis of propylene carbonate from propylene oxide and CO₂ on copper electrodes	101
6.1 Introduction	102
6.2 Experimental	103
6.3 Results and discussion.....	105
6.3.1 Cyclic voltammetry.....	105
6.3.2 FTIR and HPLC characterization of intermediates and products	106
6.3.3 Proposed mechanism	114
6.3.3 Electrosynthesis of propylene carbonate on other metals ...	119
6.4 Conclusion	120
Summary	121
References	125
Appendix I.....	141
Appendix II.....	143
Appendix III.....	147
Appendix IV.....	151
Appendix V	173
Samenvatting.....	175
Resumen.....	181
List of publications	187
Curriculum vitae	189

