



Universiteit
Leiden
The Netherlands

The electrocatalytic oxidation of ethanol studied on a molecular scale

Lai, S.S.S.

Citation

Lai, S. S. S. (2010, June 16). *The electrocatalytic oxidation of ethanol studied on a molecular scale*. Retrieved from <https://hdl.handle.net/1887/15725>

Version: Corrected Publisher's Version

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

Downloaded from: <https://hdl.handle.net/1887/15725>

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

**THE ELECTROCATALYTIC OXIDATION OF ETHANOL
STUDIED ON A MOLECULAR SCALE**

Stanley Chi Shing Lai

2010

**THE ELECTROCATALYTIC OXIDATION OF ETHANOL
STUDIED ON A MOLECULAR SCALE**

Proefschrift

ter verkrijging van
de graad van Doctor aan de Universiteit Leiden
op gezag van Rector Magnificus prof.mr. P.F. van der Heijden,
volgens besluit van het College voor Promoties
te verdedigen op woensdag 16 juni 2010
klokke 13.45 uur

door

Stanley Chi Shing Lai

geboren te 's-Gravenhage in 1982

Promotiecommissie

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

Overige leden: Prof. Dr. J. Brouwer
Prof. Dr. B.E. Nieuwenhuys
Prof. Dr. A.W. Kleyn
Prof. Dr. R. A. van Santen (Technische Universiteit Eindhoven)
Prof. Dr. R. J. Behm (Universität Ulm, Duitsland)

ISBN 978-90-8570-568-0

Printed by Wöhrmann Print Service

*Nothing is too wonderful to be true,
if it be consistent with the laws of nature*

Michael Faraday (1791-1867)

CONTENTS

1	Introduction	11
1.1	Catalysis	12
1.1.1	Catalysis and catalysts	12
1.1.2	Electrocatalysis	14
1.1.3	Model catalysts	15
1.2	Fuel cell systems	17
1.2.1	Historical overview	17
1.2.2	Basic working principle of a fuel cell	18
1.2.3	Direct ethanol fuel cell	19
1.3	Electrocatalytic oxidation of ethanol	21
1.3.1	Ethanol oxidation on platinum	21
1.3.2	Ethanol oxidation on other metals	24
1.3.3	Ethanol oxidation on bi- and trimetallic electrodes	25
1.4	Scope of this thesis	27
1.5	References	28
2	Experimental techniques	33
2.1	Electrochemical methods	34
2.1.1	Electrochemical set-up	34
2.1.2	Cyclic voltammetry	35
2.1.3	Chronoamperometry	36
2.1.4	Rotating disk electrode	37
2.2	Vibrational spectroscopy	38
2.2.1	Fourier transform infrared spectroscopy	39
2.2.2	Surface enhanced Raman spectroscopy	41
2.3	Online electrochemical mass spectrometry	42
2.4	References	45
3	Ethanol and acetaldehyde electro-oxidation on platinum single-crystal electrodes in acidic media	47
3.1	Introduction	48
3.2	Experimental	49
3.3	Results and discussion	50

3.3.1	Ethanol	50
	Continuous oxidation	50
	Adsorbate stripping	55
3.3.2	Acetaldehyde	60
	Continuous oxidation	60
	Adsorbate stripping	63
3.3.3	Acetic acid	65
3.4	General discussion	67
3.5	Conclusions	69
3.6	References	70
4	Ethanol electro-oxidation on platinum single-crystal electrodes in acidic media: an OLEMS study	73
4.1	Introduction	74
4.2	Experimental	75
4.3	Results and discussion	76
4.4	Conclusions	81
4.5	References	82
5	Ethanol and acetaldehyde dissociation and electro-oxidation on platinum: a SERS study	83
5.1	Introduction	84
5.2	Experimental	86
5.3	Results and discussion	87
	5.3.1 Cyclic voltammetry	87
	5.3.2 Surface enhanced Raman spectroscopy	91
	Ethanol	91
	Acetaldehyde	95
	Deuterated compounds	97
5.4	Mechanistic implications	101
5.5	Conclusions	102
5.6	References	103

6	Ethanol electro-oxidation on platinum in alkaline media	107
6.1	Introduction	108
6.2	Experimental	110
6.3	Results and discussion	111
6.3.1	Voltammetric studies	111
6.3.2	Surface enhanced Raman spectroscopy	122
6.4	General discussion	128
6.5	Conclusions	131
6.6	References	131
7	Effects of electrolyte pH and composition on the ethanol electro-oxidation reaction	135
7.1	Introduction	136
7.2	Experimental	138
7.3	Results and discussion	139
7.3.1	Ethanol oxidation on platinum	139
7.3.2	Ethanol oxidation on gold	155
7.4	General discussion and conclusions	159
7.5	References	163
	Summary	167
	Dutch summary (Samenvatting)	169
	Chinese summary (摘要)	171
	List of publications	173
	Curriculum vitae	175
	Nawoord	177

