



Computational Investigation of Solvation Phenomena at Metal-Electrolyte Interfaces

Oskar Cheong

Energie & Umwelt / Energy & Environment

Band / Volume 631

ISBN 978-3-95806-759-2

Forschungszentrum Jülich GmbH
Institut für Energie- und Klimaforschung (IEK)
Theorie und computergestützte Modellierung
von Materialien in der Energietechnik (IEK-13)

Computational Investigation of Solvation Phenomena at Metal-Electrolyte Interfaces

Oskar Cheong

Schriften des Forschungszentrums Jülich
Reihe Energie & Umwelt / Energy & Environment

Band / Volume 631

ISSN 1866-1793

ISBN 978-3-95806-759-2

Contents

Abstract	iii
Kurzfassung	v
Acknowledgements	vii
Declaration	ix
List of Acronyms	xi
Preface	xvii
1 Introduction	1
1.1 Electrochemical CO ₂ Reduction	1
1.2 Atomistic Simulation of Metal-Electrolyte Interface	4
1.2.1 From Gas-phase Simulations to Solvation-based Simulations	4
1.2.2 Brief Review of Solvation Models at Interfaces	6
1.3 Scope and Outline of Work	9
2 Theory and Methodology	13
2.1 Density Functional Theory	13
2.1.1 Pre-DFT: The Path to Density Functional Theory	13
2.1.2 DFT Methodology	16
2.1.3 Approximations of DFT	18
2.2 Force Field-based Molecular Dynamics	20
2.2.1 Molecular Dynamics Algorithm	20
2.2.2 Force Field for CMD	22
2.2.3 Statistical Ensembles	24

2.3	Solvation Schemes of Adsorbates at Metal-Electrolyte Interfaces	25
2.3.1	Implicit Solvation	25
2.3.2	Explicit Solvation	27
2.3.3	Hybrid Solvation	28
2.4	Calculation of Reaction Free Energy	28
2.4.1	Computational Hydrogen Electrode (CHE)	28
2.4.2	Nudged Elastic Band (NEB) Method	31
3	Water Structures on Pb(100) and (111) Surface Studied with the Interface Force Field (IFF)	33
3.1	Introduction	34
3.2	Computational Details	35
3.2.1	Classical Molecular Dynamics (CMD) Computations	35
3.2.2	Density Functional Theory (DFT) Computations	36
3.3	Results and Discussion	37
3.3.1	DFT Calculations	37
3.3.2	CMD Simulations of Single Water Layer	39
3.3.3	Surface Size Effect of Water Structure on Pb(100) Surface	44
3.3.4	CMD Simulations of Thick Water Slab	46
3.3.5	CMD Simulations of Water Structure on Pb(111)	48
3.4	Summary	49
4	Impact of Solvation Phenomena on the CO₂ Reduction Reaction at Pb(100) and Ag(100) Surfaces	51
4.1	Introduction	52
4.2	Computational Details	55
4.2.1	Density Functional Theory (DFT) Computations	55
4.2.2	Classical Molecular Dynamics (CMD) Computations	56
4.2.3	Explicit Solvation Configuration Setup	56
4.2.4	Reaction Energy Calculations	56
4.2.5	Microkinetic Modeling	58
4.3	Results	59
4.3.1	Solvation Effect on CO ₂ Reduction Reaction to HCOOH or CO at Pb(100) Surface	59

4.3.2	Reaction Energy Pathways for CO ₂ Reduction Reaction at Pb(100) and Ag(100) Surfaces	64
4.4	Discussion	69
4.4.1	Explicit Solvation Uncertainty Analysis of HCOO* and COOH* Adsorption Energy	69
4.4.2	Potential Descriptors that Affect HCOO* and COOH* Adsorption Energy in Solvation	74
4.5	Summary	77
5	Entropy Effects on Reactive Processes at Metal-Solvent Interfaces	79
5.1	Introduction	80
5.2	Methods	81
5.2.1	2PT Method	81
5.2.2	Theoretical Solvation Model	83
5.2.3	Computational Methodology	85
5.3	Results and Discussion	86
5.3.1	Bulk Water	86
5.3.2	Alcohol Molecules in Bulk Aqueous Solution	87
5.3.3	Entropy of Alcohol Molecules at Metal-Solvent Interface	89
5.3.4	Impact of Solvation Entropy on Surface Chemistry	94
5.3.5	Alcohol Molecules in Bulk Toluene	96
5.4	Summary	99
6	Conclusions and Outlook	101
A	Supporting Information for Chapter 3	127
B	Supporting Information for Chapter 4	129
C	Supporting Information for Chapter 5	135
	List of Publications	137
	Conference Contributions	139
	Contribution to Co-Author Publications	141

Energie & Umwelt / Energy & Environment
Band / Volume 631
ISBN 978-3-95806-759-2

Mitglied der Helmholtz-Gemeinschaft

