

Contents

Preface XIII

List of Contributors XV

1	Multiscale Modeling of Electrochemical Systems	1
	<i>Jonathan E. Mueller, Donato Fantauzzi, and Timo Jacob</i>	
1.1	Introduction	1
1.2	Introduction to Multiscale Modeling	3
1.3	Electronic Structure Modeling	6
1.3.1	Modern Electronic Structure Theory	6
1.3.1.1	Quantum Mechanical Foundations	6
1.3.1.2	Born–Oppenheimer Approximation	8
1.3.1.3	Single-Electron Hamiltonians	9
1.3.1.4	Basis Sets	10
1.3.1.5	Enforcing the Pauli Principle	11
1.3.1.6	Electron Correlation Methods	12
1.3.1.7	Density Functional Theory	14
1.3.2	Applications of Electronic Structure to Geometric Properties	16
1.3.2.1	Geometry Optimization	16
1.3.2.2	Transition State Searches	17
1.3.3	Corrections to Potential Energy Surfaces and Reaction Pathways	18
1.3.3.1	Energy and Entropy Corrections	18
1.3.3.2	Thermodynamic State Functions	20
1.3.3.3	Reaction Energies and Rates	21
1.3.4	Electronic Structure Models in Electrochemistry	22
1.3.4.1	Modeling the Electrode Surface: Cluster versus Slab	23
1.3.4.2	Modeling the Solvent: Explicit versus Implicit	24
1.3.4.3	Modeling the Electrode Potential	25
1.3.5	Summary	26
1.4	Molecular Simulations	27
1.4.1	Energy Terms and Force Field Parameters	27
1.4.1.1	Covalent Bond Interactions	27
1.4.1.2	Non-Covalent Interactions	32
1.4.2	Parametrization and Validation	34
1.4.3	Atomistic Simulations	35

1.4.3.1	Monte Carlo Methods	35
1.4.3.2	Molecular Dynamics	36
1.4.3.3	QM/MM	37
1.4.4	Sampling and Analysis	39
1.4.5	Applications of Molecular Modeling in Electrochemistry	39
1.4.6	Summary	40
1.5	Reaction Modeling	40
1.5.1	Introduction	40
1.5.2	Chemical Kinetics	41
1.5.3	Kinetic Monte Carlo	41
1.5.3.1	System States and the Lattice Approximation	41
1.5.3.2	Reaction Rates	42
1.5.3.3	Reaction Dynamics	43
1.5.3.4	Applications of kMC in Electrochemistry	45
1.5.4	Summary	45
1.6	The Oxygen Reduction Reaction on Pt(111)	46
1.6.1	Introduction to the Oxygen Reduction Reaction	46
1.6.2	Preliminary Considerations	46
1.6.3	DFT Calculations	48
1.6.4	Method Validation	49
1.6.5	Reaction Energies	49
1.6.6	Solvation Effects	51
1.6.7	Free Energy Contributions	52
1.6.8	Influence of an Electrode Potential	53
1.6.9	Modeling the Kinetic Rates	55
1.6.10	Summary	58
1.7	Formic Acid Oxidation on Pt(111)	59
1.7.1	Introduction to Formic Acid Oxidation	59
1.7.2	Density Functional Theory Calculations	60
1.7.3	Gas Phase Reactions	60
1.7.4	Explicit Solvation Model	61
1.7.5	Eley–Rideal Mechanisms and the Electrode Potential	63
1.7.6	Kinetic Rate Model of Formic Acid Oxidation	65
1.7.7	Summary	66
1.8	Concluding Remarks	66
	References	67
2	Statistical Mechanics and Kinetic Modeling of Electrochemical Reactions on Single-Crystal Electrodes Using the Lattice-Gas Approximation	75
	<i>Marc T.M. Koper</i>	
2.1	Introduction	75
2.2	Lattice-Gas Modeling of Electrochemical Surface Reactions	76
2.3	Statistical Mechanics and Approximations	79
2.3.1	Static System	79
2.3.2	Dynamical System	83

2.4	Monte Carlo Simulations	84
2.5	Applications to Electrosorption, Electrodeposition and Electrocatalysis	85
2.5.1	Electrosorption and Electrodeposition	85
2.5.2	Electrocatalysis	92
2.6	Conclusions	96
	References	96
3	Single Molecular Electrochemistry within an STM	99
	<i>Richard J. Nichols and Simon J. Higgins</i>	
3.1	Introduction	99
3.2	Experimental Methods for Single Molecule Electrical Measurements in Electrochemical Environments	101
3.3	Electron Transfer Mechanisms	103
3.3.1	Tunneling	106
3.3.2	Resonant Tunneling	109
3.3.3	Hopping Models	111
3.4	Single Molecule Electrochemical Studies with an STM	115
3.4.1	Adsorbed Iron Complexes	115
3.4.2	Viologens	118
3.4.3	Osmium and Cobalt Metal Complexes	122
3.4.4	PyrroloTTF (pTTF)	125
3.4.5	Perylene Tetracarboxylic Diimides	128
3.4.6	Oligo(phenylene ethynylene) Derivates	130
3.5	Conclusions and Outlook	131
	References	134
4	From Microbial Bioelectrocatalysis to Microbial Bioelectrochemical Systems	137
	<i>Uwe Schröder and Falk Harnisch</i>	
4.1	Prelude: From Fundamentals to Biotechnology	137
4.2	Microbial Bioelectrochemical Systems (BESs)	137
4.2.1	The Archetype: Microbial Fuel Cells (MFCs)	137
4.2.2	Strength Through Diversity: Microbial Bioelectrochemical Systems	139
4.3	Bioelectrocatalysis: Microorganisms Catalyze Electrochemical Reactions	140
4.3.1	Energetic Considerations of Microbial Bioelectrocatalysis	141
4.3.1.1	Case Study: The Anodic Acetate Oxidation by <i>Geobacteraceae</i>	142
4.3.1.2	Case Study: The Cathodic Hydrogen Evolution Reaction (HER)	143
4.3.2	Microbial Electron Transfer Mechanisms	144
4.3.2.1	Direct Electron Transfer (DET)	144
4.3.2.2	Mediated Electron Transfer (MET)	146
4.3.2.3	Cathodic Electron Transfer Mechanisms	148
4.3.3	Microbial Interactions: Ecological Networks	148

4.3.3.1	Interspecies Electron Transfer and “Scavenging” of Redox-Shuttles	148
4.4	Characterizing Anodic Biofilms by Electrochemical and Biological Means	149
4.4.1.1	Case Study: On the use of Cyclic Voltammetry	154
4.4.1.2	Case Study: Raman Microscopy	155
	References	156
5	Electrocapillarity of Solids and its Impact on Heterogeneous Catalysis	163
	<i>Jörg Weissmüller</i>	
5.1	Introduction	163
5.2	Mechanics of Solid Electrodes	164
5.2.1	Outline – Surface Stress and Surface Tension	164
5.2.2	Solid Versus Fluid	167
5.2.3	Free Energy of Elastic Solid Surfaces	167
5.2.4	Deforming a Solid Surface	170
5.2.5	Case Study: Thought Experiment in Electrowetting	172
5.2.6	Capillary Equations for Fluids and Solids	175
5.2.7	Case Study: Molecular Dynamics Study of Surface-Induced Pressure	177
5.3	Electrocapillary Coupling at Equilibrium	177
5.3.1	Outline – Polarizable and Nonpolarizable Electrodes	177
5.3.2	Lippmann Equation and Electrocapillary Coupling Coefficient	179
5.3.3	Case Study: Cantilever-Bending Experiment in Electrolyte	181
5.3.4	Important Maxwell Relations for Electrocapillarity	183
5.3.5	Electrocapillary Coupling During Electrosorption	184
5.3.6	Coupling Coefficient for Adsorption from Gas	185
5.3.7	Coupling Coefficient for the Langmuir Isotherm	186
5.3.8	Case Study: Strain-Dependent Hydrogen Underpotential Deposition	187
5.3.9	Coupling Coefficient for Potential of Zero Charge and Work Function	190
5.3.10	Empirical Data for the Electrocapillary Coupling Coefficient	193
5.4	Exploring the Dynamics	198
5.4.1	Outline	198
5.4.2	Cyclic Cantilever-Bending Experiments	199
5.4.3	Dynamic Electro-Chemo-Mechanical Analysis	200
5.5	Mechanically Modulated Catalysis	203
5.5.1	Outline	203
5.5.2	Phenomenology; Distinguishing Capacitive from Faraday Current	204
5.5.3	Rate equations: Butler–Volmer kinetics	206
5.5.4	Rate Equations: Heyrowsky Reaction	207
5.6	Summary and Outlook	212
	References	215

6	Synthesis of Precious Metal Nanoparticles with High Surface Energy and High Electrocatalytic Activity	221
	<i>Long Huang, Zhi-You Zhou, Na Tian, and Shi-Gang Sun</i>	
6.1	Introduction	221
6.2	Shape-Controlled Synthesis of Monometallic Nanocrystals with High Surface Energy	224
6.2.1	Electrochemical Route	224
6.2.1.1	Platinum	224
6.2.1.2	Palladium	228
6.2.2	Wet-Chemical Route	230
6.2.2.1	Platinum	230
6.2.2.2	Palladium	232
6.2.2.3	Gold	234
6.3	Shape-Controlled Synthesis of Bimetallic NCs with High Surface Energy	235
6.3.1	Surface Modification	236
6.3.1.1	Bi-Modified THH Pt NCs	237
6.3.1.2	Ru-Modified THH Pt NCs	239
6.3.1.3	Au-Modified Pt THH NCs	241
6.3.1.4	Pt-Modified Au Prisms with High-Index Facets	243
6.3.2	Alloy NCs	245
6.3.2.1	THH PdPt Alloy	245
6.3.2.2	HOH PdAu Alloy	247
6.3.3	Core–Shell Structured NCs	248
6.4	Concluding Remarks and Perspective	254
	References	256
7	X-Ray Studies of Strained Catalytic Dealloyed Pt Surfaces	259
	<i>Peter Strasser</i>	
7.1	Introduction	259
7.2	Dealloyed Bimetallic Surfaces	262
7.3	Dealloyed Strained Pt Core–Shell Model Surfaces	264
7.4	X-Ray Studies of Dealloyed Strained PtCu ₃ (111) Single Crystal Surfaces	266
7.5	X-Ray Studies of Dealloyed Strained Pt–Cu Polycrystalline Thin Film Surfaces	269
7.6	X-Ray Studies of Dealloyed Strained Alloy Nanoparticles	273
7.6.1	Bragg Brentano Powder X-Ray Diffraction (XRD)	273
7.6.2	<i>In Situ</i> High Temperature Powder X-Ray Diffraction (XRD)	274
7.6.3	Synchrotron X-Ray Photoemission Spectroscopy (XPS)	276
7.6.4	Anomalous Small Angle X-Ray Scattering (ASAXS)	277
7.6.5	Anomalous Powder X-Ray Diffraction (AXRD)	277

7.6.6	High Energy X-Ray Diffraction (HE-XRD) and Atomic Pair Distribution Function (PDF) Analysis	281
7.7	Conclusions	284
	References	285

Index 293