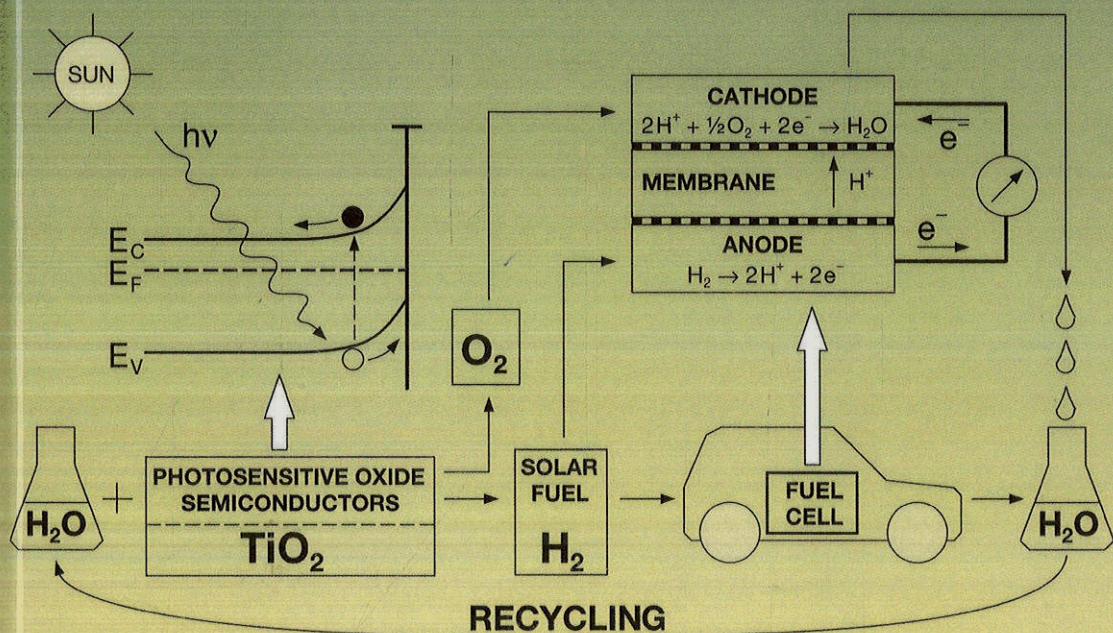


# Oxide Semiconductors for Solar Energy Conversion

## Titanium Dioxide



Janusz Nowotny

---

# Contents

Series Preface.....	xiii
Foreword.....	xv
Foreword.....	xvii
Preface.....	xix
Notation.....	xxiii
Introduction.....	xxvii

<b>Chapter 1</b>	<b>Solid-State Electrochemistry of Binary Metal Oxides .....</b>	<b>1</b>
1.1	Structural Defects.....	1
1.1.1	Thermodynamically Irreversible Defects .....	1
1.1.2	Point Defects .....	4
1.2	Nonstoichiometry .....	4
1.3	Point Defects in Binary Metal Oxides.....	6
1.3.1	Types of Defects .....	6
1.3.2	Thermodynamic Approach .....	8
1.3.3	Defect Reactions.....	9
1.3.3.1	General Rules .....	9
1.3.3.2	Defect Equilibria .....	9
1.3.3.3	Stoichiometric Oxides .....	11
1.3.3.4	Nonstoichiometric Oxides .....	12
1.3.3.5	Brouwer-Type Diagrams .....	15
1.3.3.6	Effect of Aliovalent Ions (Donors and Acceptors) .....	16
1.3.4	Defects Aggregation.....	27
1.3.5	Dispersed Systems.....	29
1.4	Band Model .....	31
1.5	Electrical Properties .....	36
1.5.1	Electrical Conductivity.....	38
1.5.1.1	Effect of Oxygen Activity.....	38
1.5.1.2	Effect of Temperature.....	42
1.5.1.3	Transference Numbers.....	44
1.5.1.4	Impedance Spectroscopy.....	45
1.5.2	Thermoelectric Power .....	45
1.5.3	Electrical Conductivity versus Thermoelectric Power Jonker Analysis.....	51
1.5.4	Work Function.....	53
1.5.4.1	Basic Terms.....	53
1.5.4.2	Work Function at Elevated Temperatures .....	57

	1.5.5	Surface Photovoltage Spectroscopy .....	62
	1.5.6	Hall Effect .....	62
	1.5.7	Coulometric Titration .....	63
1.6		Effect of Interfaces .....	65
	1.6.1	Surface Reactivity .....	65
	1.6.2	Surface Sensitive Tools .....	67
	1.6.3	Surface Segregation .....	69
		1.6.3.1 Impurities .....	72
		1.6.3.2 Low-Dimensional Structures.....	72
		1.6.3.3 Oxygen Activity .....	72
		1.6.3.4 Segregation of Intrinsic Defects .....	72
	1.6.4	Surface versus Bulk Properties .....	73
		1.6.4.1 Examples of NiO and CoO .....	75
		1.6.4.2 Examples of NiO and CoO Solid Solutions .....	78
		1.6.4.3 Low-Dimensional Interface Structures .....	86
1.7		Diffusion .....	87
	1.7.1	Diffusion Mechanisms .....	87
		1.7.1.1 Vacancy Mechanism .....	87
		1.7.1.2 Interstitial Mechanism .....	87
		1.7.1.3 Interstitialcy Mechanism (Collinear).....	88
		1.7.1.4 Interstitialcy Mechanism (Noncollinear).....	88
		1.7.1.5 Interface Diffusion.....	88
	1.7.2	Diffusion Kinetics .....	89
	1.7.3	Grain Boundary Diffusion .....	93
	1.7.4	Chemical Diffusion .....	95
		1.7.4.1 Gas/Solid Equilibration .....	95
		1.7.4.2 Bulk Diffusion Controlled Kinetics .....	99
		1.7.4.3 Segregation-Induced Diffusive Resistance .....	102
		1.7.4.4 Monitoring of Gas/Solid Kinetics.....	105
		1.7.4.5 Relationships between Diffusion Coefficients .....	108
1.8		Oxygen Ion Conductors .....	110
	1.8.1	Electronic versus Ionic Conductors.....	110
	1.8.2	Electrochemical Cells .....	110
	1.8.3	Oxidation Mechanism .....	114
1.9		Brief Survey on Selected Oxides.....	117
1.10		Concluding Remarks .....	118
		References .....	119
		Assignable Problems .....	125
<b>Chapter 2</b>		<b>Light-Induced Effects.....</b>	<b>127</b>
	2.1	Solar Radiation .....	127
	2.2	Solar Energy Spectrum .....	127

2.3	Light Source .....	132
2.4	Light-Induced Effects in Semiconductors .....	132
2.5	Data Reproducibility .....	134
2.6	Energy Conversion Efficiency .....	135
2.6.1	Basic Relationships.....	135
2.6.2	Energy Losses .....	138
2.6.2.1	Interdependence of Functional Properties...	139
2.7	Light Measurements .....	140
2.8	Concluding Remarks .....	141
	References .....	141
	Assignable Problems .....	143
<b>Chapter 3</b>	<b>Basic Properties of TiO<sub>2</sub>.....</b>	<b>145</b>
3.1	Titanium Oxides .....	145
3.2	Titanium Dioxide.....	145
3.2.1	Occurrence, Application, and Properties .....	145
3.2.2	Nonstoichiometry .....	146
3.2.3	Production .....	147
3.2.4	Structure .....	148
3.2.5	Phase Diagram and Structures .....	151
3.2.6	Shear Structures .....	153
3.2.7	Electronic Structure .....	155
3.2.8	Anisotropy of Rutile.....	158
3.2.8.1	Electrical Resistivity.....	159
3.2.8.2	Diffusion Kinetics .....	159
3.3	Concluding Remarks .....	160
	References .....	160
	Assignable Problems .....	163
<b>Chapter 4</b>	<b>Defect Chemistry .....</b>	<b>165</b>
4.1	Undoped Titanium Dioxide .....	165
4.1.1	Point Defects in TiO <sub>2</sub> .....	165
4.1.2	Nonstoichiometry .....	166
4.1.3	Defect Reactions.....	167
4.1.4	Brouwer Defect Diagrams.....	171
4.1.5	Full Defect Diagram.....	175
4.1.6	Anomalies .....	178
4.1.7	Effect of Cooling.....	179
4.1.8	Effect of Oxygen on Fermi Level.....	180
4.2	Doping with Aliovalent Ions .....	183
4.2.1	Cations versus Anions .....	183
4.2.2	Donor-Doped TiO <sub>2</sub> .....	184
4.2.3	Acceptor-Doped TiO <sub>2</sub> .....	186
4.3	Reactivity of Titanium Dioxide with Hydrogen.....	193

4.4	Real Chemical Formula of $\text{TiO}_2$ .....	199
4.5	Concluding Remarks .....	202
	References .....	203
	Assignable Problems .....	205
<b>Chapter 5</b>	<b>Electrical Properties .....</b>	<b>207</b>
5.1	Introduction .....	207
5.2	Electrical Conductivity.....	207
5.2.1	General .....	207
5.2.2	Undoped $\text{TiO}_2$ .....	208
5.2.2.1	Effect of Oxygen Activity .....	210
5.2.2.2	Effect of Temperature .....	216
5.2.2.3	Mobility Terms .....	222
5.2.2.4	Transference Numbers .....	224
5.2.2.5	Electrical Conductivity Components .....	226
5.2.2.6	Effect of Impurities.....	229
5.2.2.7	Effect of Cooling .....	230
5.2.3	Donor-Doped $\text{TiO}_2$ .....	232
5.2.4	Acceptor-Doped $\text{TiO}_2$ .....	239
5.2.5	Heterogeneous Doping of $\text{TiO}_2$ .....	241
5.3	Thermoelectric Power .....	242
5.4	Jonker Analysis.....	255
5.5	Work Function .....	259
5.6	Surface Photovoltage Spectroscopy .....	263
5.7	Hall Effect .....	264
5.8	Coulometric Titration .....	265
5.9	Concluding Remarks .....	266
	References .....	267
	Assignable Problems .....	272
<b>Chapter 6</b>	<b>Diffusion.....</b>	<b>275</b>
6.1	Mass Transport Kinetics.....	275
6.2	Self-Diffusion .....	275
6.3	Chemical Diffusion .....	280
6.3.1	Equilibration Kinetics .....	280
6.3.2	Double Equilibration Kinetics.....	286
6.3.3	Nb-doped $\text{TiO}_2$ .....	288
6.3.4	Alternative Diffusion Models.....	291
6.4	Concluding Remarks .....	294
	References .....	295
	Assignable Problems .....	297
<b>Chapter 7</b>	<b>Effect of Interfaces .....</b>	<b>299</b>
7.1	Effect of Surface Properties on Reactivity.....	299

7.1.1	Introduction .....	299
7.1.2	Surface Science Approach .....	299
7.2	Segregation .....	304
7.3	Reactivity .....	309
7.3.1	Reactivity of TiO <sub>2</sub> with Light .....	309
7.3.2	Reactivity and Photoreactivity of TiO <sub>2</sub> with Oxygen and Water .....	310
7.3.2.1	Oxygen .....	310
7.3.2.2	Water .....	311
7.3.3	Collective and Local Reactivity Factors .....	312
7.4	Concluding Remarks .....	318
	References .....	319
	Assignable Problems .....	322
<b>Chapter 8</b>	<b>Applications.....</b>	<b>323</b>
8.1	Introduction .....	323
8.2	Performance-Related Properties .....	324
8.2.1	Electronic Structure .....	325
8.2.2	Flat Band Potential .....	327
8.2.3	Charge Transport.....	330
8.2.4	Surface Active Sites.....	330
8.2.5	Surface versus Bulk Properties .....	331
8.3	Solar Hydrogen .....	332
8.3.1	Solar-to-Hydrogen Pathways .....	332
8.3.2	Solar Water Splitting in Nature .....	334
8.3.3	Environmental Aspects .....	335
8.3.4	Cost-Related Aspects .....	338
8.4	Hydrogen Generation by Photoelectrochemical Water Splitting .....	338
8.4.1	General Concept.....	339
8.4.2	Reactions in Photoelectrochemical Cells .....	342
8.4.3	Band Model of Photoelectrochemical Cells.....	343
8.4.4	Photocell Structures .....	346
8.4.4.1	Photoelectrochemical Cell Equipped with One Photoelectrode .....	347
8.4.4.2	Hybrid-Type Cells.....	347
8.4.4.3	Photoelectrochemical Cell Equipped with Two Photoelectrodes.....	349
8.4.4.4	Alternative Solutions .....	352
8.4.5	Simple Comparisons .....	353
8.4.6	Hurdles to Commercialization .....	354
8.4.6.1	Potential Market .....	354
8.4.6.2	Multidisciplinary Approach.....	354
8.5	Solar Water Purification .....	356
8.5.1	Significance and Basic Concepts.....	356

8.5.2	Photoreactivity of $\text{TiO}_2$ with Water .....	358
8.5.2.1	Anodic Site .....	358
8.5.2.2	Cathodic Site.....	360
8.5.3	Modification of Photocatalytic Properties .....	361
8.5.3.1	Deposition of Noble Metals .....	361
8.5.3.2	Doping with Aliovalent Ions.....	362
8.5.4	Unresolved Problems.....	362
8.5.5	Oxidation of Microorganisms .....	365
8.6	Alternative Applications.....	371
8.7	Concluding Remarks .....	372
8.7.1	Research Progress and Perspectives.....	374
	References .....	375
	Assignable Problems .....	381
Appendix.....		383
	Fundamental Constants .....	383
	Selected Conversion Factors .....	383
	Selected Definitions.....	383
	Conversion Prefixes.....	384
Index .....		385