

# Contents

<b>1</b>	<b>Introduction</b>	<b>1</b>
1.1	Introductory Words to Mixed Diffusion and Interface Control	1
1.2	Glossarial Explanation of Terminologies Relevant to Interfacial Reaction and Diffusion	3
1.3	Remarks for Further Consideration	6
1.4	Concluding Remarks	8
	References	9
<b>2</b>	<b>Electrochemical Methods</b>	<b>11</b>
2.1	Chronopotentiometry	11
2.2	Chronoamperometry	16
2.3	Voltammetry	20
2.4	Electrochemical Impedance Spectroscopy	25
	References	30
<b>3</b>	<b>Hydrogen Absorption into and Subsequent Diffusion Through Hydride-Forming Metals</b>	<b>33</b>
3.1	Introduction	33
3.2	Transmission Line Model Describing Overall Hydrogen Insertion	35
3.3	Faradaic Admittance Involving Hydrogen Absorption Reaction ( <i>HAR</i> ) into and Subsequent Diffusion Through Hydride-Forming Metals	42
3.3.1	Transmissive Permeable ( <i>PB</i> ) Boundary Condition	46
3.3.2	(i) Model A – Indirect (Two-Step) Hydrogen Absorption Reaction ( <i>HAR</i> ) Through Adsorbed Phase (State) – (a) Diffusion-Controlled <i>HAR</i> Limit and – (b) Interface-Controlled <i>HAR</i> Limit	48
3.3.3	(i) – (a) Diffusion-Controlled <i>HAR</i> Limit	54
3.3.4	(i) – (b) Interface-Controlled <i>HAR</i> Limit	56
3.3.5	(ii) Model B: Direct (One-Step) Hydrogen Absorption Reaction ( <i>HAR</i> ) Without Adsorbed Phase (State)	59
3.3.6	(iii) Comparison of Simulation with Experimental Results	63

3.3.7	Reflective Impermeable ( <i>IPB</i> ) Boundary Condition . . . . .	66
3.3.8	Evidence for Direct (One-Step) Hydrogen Absorption Reaction ( <i>HAR</i> ) and the Indirect to Direct Transition in <i>HAR</i> Mechanism . . . . .	72
3.4	Summary and Concluding Remarks . . . . .	78
	References . . . . .	78
<b>4</b>	<b>Hydrogen Transport Under Impermeable Boundary Conditions . .</b>	<b>83</b>
4.1	Redox Reactions of Hydrogen Injection and Extraction . . . . .	83
4.2	Concept of Diffusion-Controlled Hydrogen Transport . . . . .	86
4.3	Diffusion-Controlled Hydrogen Transport in the Presence of Single Phase . . . . .	87
4.3.1	Flat Electrode Surface . . . . .	87
4.3.2	Rough Electrode Surface . . . . .	91
4.3.3	Effect of Diffusion Length Distribution . . . . .	95
4.4	Diffusion-Controlled Hydrogen Transport in the Case Where Two Phases Coexist . . . . .	96
4.4.1	Diffusion-Controlled Phase Boundary Movement in the Case Where Two Phases Coexist . . . . .	96
4.4.2	Diffusion-Controlled Phase Boundary Movement Coupled with Boundary Pining . . . . .	99
	References . . . . .	102
<b>5</b>	<b>Hydrogen Trapping Inside Metals and Metal Oxides . . . . .</b>	<b>105</b>
5.1	Hydrogen Trapping in Insertion Electrodes: Modified Diffusion Equation . . . . .	106
5.2	Hydrogen Trapping Determined by Current Transient Technique	108
5.3	Hydrogen Trapping Determined by Ac-Impedance Technique . .	114
	References . . . . .	119
<b>6</b>	<b>Generation of Internal Stress During Hydrogen and Lithium Transport . . . . .</b>	<b>123</b>
6.1	Relationship Between Diffusion and Macroscopic Deformation .	123
6.1.1	Elasto-Diffusive Phenomenon . . . . .	123
6.1.2	Diffusion-Elastic Phenomenon . . . . .	125
6.2	Theory of Stress Change Measurements . . . . .	125
6.2.1	Laser Beam Deflection ( <i>LBD</i> ) Method . . . . .	125
6.2.2	Double Quartz Crystal Resonator ( <i>DQCR</i> ) Method . . . .	128
6.3	Setups for the Stress Change Measurements . . . . .	131
6.3.1	<i>LBD</i> Method . . . . .	131
6.3.2	<i>DQCR</i> Method . . . . .	132
6.4	Interpretation of Insertion-Induced Internal Stress . . . . .	134
6.4.1	Analysis of <i>LBD</i> Results . . . . .	134
6.4.2	Analysis of <i>DQCR</i> Results . . . . .	143
	References . . . . .	145

<b>7</b>	<b>Abnormal Behaviors in Hydrogen Transport: Importance of Interfacial Reactions</b>	149
7.1	Interfacial Reactions Involved in Hydrogen Transport	149
7.2	Hydrogen Diffusion Coupled with the Charge Transfer Reaction	150
7.2.1	Flat Electrode Surface	150
7.2.2	Rough Electrode Surface	157
7.3	Hydrogen Diffusion Coupled with the Hydrogen Transfer Reaction	159
7.4	Change in Boundary Condition with Driving Force for Hydrogen Transport	166
7.4.1	Effect of Ohmic Potential Drop	166
7.4.2	Effect of Potential Step	167
7.4.3	Effect of Surface Properties	168
	References	170
<b>8</b>	<b>Effect of Cell Impedance on Lithium Transport</b>	173
8.1	Anomalous Features of Lithium Transport	173
8.1.1	Non-Cottrell Behavior at the Initial Stage of Lithium Transport	173
8.1.2	Discrepancy Between Anodic and Cathodic Behaviors	175
8.1.3	Quasi-constant Current During Phase Transition	176
8.1.4	Lower Initial Current Level at Larger Potential Step	179
8.2	Revisiting the Governing Mechanism of Lithium Transport	182
8.2.1	Ohmic Relationship at the Initial Stage of Lithium Transport	182
8.2.2	Validity of Ohmic Relationship throughout the Lithium Transport Process	182
8.2.3	Origin for Quasi-Constant Current and Suppressed Initial Current	185
8.2.4	Validation of Internal Cell Resistance Obtained from Chronoamperometry	186
8.3	Theoretical Consideration of “Cell-Impedance-Controlled” Lithium Transport	188
8.3.1	Model for Chronoamperometry	188
8.3.2	Lithium Transport in the Single-Phase Region	190
8.3.3	Lithium Transport with Phase Transition	192
8.4	Analysis of Lithium Transport Governed by Cell Impedance	194
8.4.1	Theoretical Reproduction of Experimental Current Transients	194
8.4.2	Parametric Dependence of Current Transients	202
8.4.3	Theoretical Current-Time Relation	204
8.4.4	Cyclic Voltammograms	206
	References	209

<b>9 Lithium Transport Through Electrode with Irregular/Partially Inactive Interfaces . . . . .</b>	<b>213</b>
9.1 Quantification of the Surface Irregularity/Inactiveness Based on Fractal Geometry . . . . .	213
9.1.1 Introduction to Fractal Geometry . . . . .	213
9.1.2 Characterization of Surface Using Fractal Geometry . . . . .	216
9.2 Theory of the Diffusion toward and from a Fractal Electrode . . . . .	219
9.2.1 Mathematical Equations . . . . .	219
9.2.2 Diffusion toward and from a Fractal Interface Coupled with a Facile Charge-Transfer Reaction . . . . .	221
9.2.3 Diffusion toward and from a Fractal Interface Coupled with a Sluggish Charge-Transfer Reaction . . . . .	225
9.3 Application of Fractal Geometry to the Analysis of Lithium Transport . . . . .	227
9.3.1 Lithium Transport through Irregular Interface . . . . .	227
9.3.2 Lithium Transport through Partially Inactive Interface . . . . .	229
References . . . . .	232
<b>About the Authors . . . . .</b>	<b>239</b>
<b>About the Editor . . . . .</b>	<b>243</b>
<b>Index . . . . .</b>	<b>245</b>