

Contents

1	Basic Principles of Nonlinear Dynamics	1
1.1	Concise Vocabulary of Nonlinear Dynamics	1
1.2	Types of Stability	5
1.3	Linear Stability Analysis	8
1.3.1	Stability of One-Dimensional Homogeneous System	8
1.3.2	Stability of Two-Dimensional Homogeneous System	14
1.3.3	The Hopf Bifurcation	25
1.3.4	The Saddle–Node Bifurcation	31
1.3.5	The Cross-Shaped Bifurcation Diagram	33
1.4	Global Bifurcations Leading to Oscillations	34
1.4.1	Saddle–Node Bifurcation of Cycles	35
1.4.2	Saddle–Node Infinite Period (SNIPER) Bifurcation	36
1.4.3	Saddle–Loop (Homoclinic) Bifurcation	37
1.5	Nullcline Representation of Dynamical Systems	38
1.6	Fast and Slow Dynamical Variables	42
1.7	Canard Explosion	50
1.8	The Activator–Inhibitor Systems	52
1.8.1	The Concept of the Activator and the Inhibitor	52
1.8.2	Correlation Between the Nullclines and the Properties of the Jacobian Matrix	54
1.9	The Existence of Closed Trajectories—The Poincaré–Bendixson Theorem	55
1.10	The Stability of the N -Dimensional Dynamical System	57
1.10.1	Linear Stability Analysis of N -Dimensional Dynamical System	57
1.10.2	Complex Periodic Behavior and Routes to Chaos in N -Dimensional Systems	60
1.10.3	Control of Chaos	68
	References	72

2	Stability of Electrochemical Systems	75
2.1	The Role of Negative Differential Resistance in the Stability of Electrochemical Systems	75
2.1.1	The Load Line and the Simplest Electrochemical Circuit	75
2.1.2	Stability of the N-NDR System Under Potentiostatic Control	76
2.1.3	Stability of N-NDR System Under Galvanostatic Control	79
2.1.4	Origins of NDR in Electrochemical Systems	80
2.1.5	Comparison of N-NDR and S-NDR Characteristics	82
2.2	Stability of a Realistic Electrochemical N-NDR System	83
2.2.1	Linear Stability Analysis of 1D Electrochemical System	83
2.2.2	Linear Stability Analysis of 2D Electrochemical System	88
2.2.3	The Advantage of Dimensionless Representation	93
2.2.4	The Electrode Potential as an Autocatalytic Variable in the N-NDR Systems	96
2.2.5	The Electrode Potential as a Negative Feedback Variable in S-NDR Systems	99
2.3	Essential and Non-essential Variables in Electrochemical Instabilities	102
2.4	Frequency of Oscillations in the N-NDR Systems	105
	References	108
3	Application of Impedance Spectroscopy to Electrochemical Instabilities	111
3.1	Outline Concept of Impedance of Electrochemical Systems	111
3.1.1	Basic Definitions	111
3.1.2	Kramers–Kronig Transforms and Electrochemical Instabilities	116
3.2	The Impedance of the Streaming Mercury Electrode	117
3.3	Application of Impedance to the Diagnosis of Stability of Electrochemical Systems	125
3.3.1	Positive and Negative Elements in Impedance Characteristics	125
3.3.2	Diagnosis of Bifurcations from Impedance Spectra	128
3.4	Impedance Characteristics of N-NDR and HN-NDR Systems	133
3.4.1	The Hidden Negative Impedance	133
3.4.2	Mechanisms Underlying the HN-NDR Oscillator	137
3.5	Classification of Electrochemical Oscillators Based on Impedance Characteristics	148
3.6	Instabilities Involving Adsorption on Electrodes	156
3.6.1	The Frumkin Isotherm	156
3.6.2	Model Mechanisms Involving Strong Adsorption	157

3.7	The Advantages of Zero-Pole Representation of Impedance for the Stability Analysis	174
3.8	Application of the Dynamic Electrochemical Impedance Spectroscopy to Electrochemical Instabilities	183
3.9	Impedance Spectroscopy and Electrochemical Pattern Formation	187
	References	190
4	Temporal Instabilities in Cathodic Processes at Liquid and Solid Electrodes	197
4.1	Electroreduction of Peroxodisulfate Ions	197
4.1.1	The N-NDR Region as a Double Layer Effect	197
4.1.2	Bifurcation Analysis	201
4.1.3	Mechanistic Aspects of $S_2O_8^{2-}$ Electroreduction	208
4.1.4	Studies at High Ionic Strength	212
4.2	Electroreduction of Iodate(V) Ions	217
4.2.1	The Role of Additional Current Carrier in the Onset of Instabilities	217
4.2.2	The NDR-Based vs. the Electrochemical Reactions and Diffusion-Convection Approach	225
4.3	The Indium-Thiocyanate Polarographic Oscillator	229
4.3.1	Basic Experimental Characteristics of In(III)-SCN ⁻ Oscillator	229
4.3.2	Models of the In(III)-SCN ⁻ Polarographic Oscillator	233
4.4	Oscillations and Bistability in the Nickel(II)-SCN ⁻ Electroreduction	249
4.4.1	Origin of the N-NDR Region in the Ni(II)-SCN ⁻ Electroreduction	249
4.4.2	Oscillations at the HMDE	251
4.4.3	Oscillations and Bistability at the Streaming Mercury Electrode	255
4.5	Tristability in the Ni(II)-N ₃ ⁻ System	276
4.5.1	Two N-NDR Regions as a Source of Tristability	276
4.5.2	The Source of Two N-NDR Regions in the Ni(II)-N ₃ ⁻ Electroreduction	279
4.5.3	Linear Stability Analysis of the Ni(II)-N ₃ ⁻ Electroreduction	284
4.5.4	Impedance Studies of the Ni(II)-N ₃ ⁻ Electroreduction	286
4.6	Oscillations in Polarographic Processes Inhibited by Surfactants	289
4.6.1	The Cu ²⁺ -Tribenzylamine Oscillator	289
4.6.2	The Mathematical Model of the "Inhibitor Oscillator"	292
4.7	Oscillatory Reduction of Hydrogen Peroxide	294
4.7.1	Oscillations on Metal Electrodes	294
4.7.2	Oscillatory Reduction of H ₂ O ₂ on Semiconductor Electrodes	308
	References	321

5	Temporal Instabilities in Anodic Oxidation of Small Molecules/Ions at Solid Electrodes	327
5.1	Oscillations in Anodic Oxidation of Molecular Hydrogen	327
5.1.1	Experimental Results and Oscillation Mechanism	327
5.1.2	Modeling the Galvanostatic Oscillations	335
5.1.3	Experimental Observation and Modeling the Potentiostatic Oscillations	340
5.2	Oscillations in Anodic Oxidation of Carbon Monoxide	345
5.3	Bistability and Oscillations in Anodic Oxidation of $H_2 + CO$ Mixture	354
5.4	Instabilities in the Anodic Oxidation of Formate Ions	357
5.4.1	Experimental Results and Outline Oscillation Mechanism	357
5.4.2	The Model of Oscillations Under Potentiostatic Conditions	363
5.4.3	The Oxidation of Formic Acid as the System of Two Suboscillators	370
5.4.4	Mechanism of Oscillations Under Galvanostatic Conditions	374
5.4.5	Recent Suggestions for the Formic Acid Oxidation Mechanism	375
5.4.6	Temperature Overcompensation Effect in Formic Acid Oxidation	376
5.4.7	Oxidation of Formic Acid as an Analog of the Stimulus–Response of Neuronal Cells	379
5.5	Oscillatory Oxidation of Formaldehyde	382
5.6	Instabilities in the Anodic Oxidation of Alcohols	392
5.6.1	Oscillations in Alcohols Oxidation	392
5.6.2	Multistability and Excitability in Alcohols Oxidation	399
5.7	Oscillatory Oxidation of Sulfur Compounds	408
5.8	Other Oscillatory Oxidation Reactions	414
	References	417
6	Temporal Instabilities in Corrosion Processes	425
6.1	Oscillations in Anodic Dissolution of Metal Electrodes	425
6.1.1	General Characteristics of Passivation/Dissolution Processes	425
6.1.2	The Fe/H_2SO_4 Oscillatory System	434
6.1.3	The Oscillatory Electrodeposition of Copper	454
6.1.4	Oscillatory Dissolution of Nickel in H_2SO_4 Medium	473
6.1.5	Oscillatory Oxidation of Cobalt Electrodes	485
6.1.6	Oscillatory Oxidation of Vanadium Electrodes	489
6.1.7	Oscillatory Dissolution of Other Metals	492
6.2	Application of Metal Electrodeposition Processes in Micromachining	501

6.3 Anodic Oscillatory Dissolution of Semiconductor Electrodes . . . 504

6.3.1 Cadmium-Based Semiconductors 504

6.3.2 Silicon in Fluoride Media 506

References 511

About the Author 521

About the Editor 523

Index 525

Contents for Volume II

1	Theoretical Background of Spatial and Spatiotemporal Patterns in Dynamical Systems	1
1.1	Chemical Reaction–Diffusion Systems	1
1.1.1	Basic Characteristics of Spatiotemporal Instabilities	1
1.1.2	Spatiotemporal Patterns in Excitable Chemical Media	3
1.1.3	Linear Stability Analysis of the Reaction–Diffusion Systems	13
1.1.4	The Turing Bifurcation	25
1.2	Electrochemical Reaction-Migration Systems	32
1.2.1	Spatial Inhomogeneities in Electrochemical Systems	32
1.2.2	Types of Spatial Coupling in Spatially Extended Electrochemical Systems	34
1.2.3	The Interaction of Spatial Couplings with the NDR Systems	47
	References	60
2	Experimental and Model Spatiotemporal and Spatial Patterns in Electrochemical Systems	65
2.1	Simple Examples of Dissipative Pattern Formation	65
2.2	Patterns in $\text{S}_2\text{O}_8^{2-}$ Electroreduction	72
2.3	Patterns in Co Electrodissolution	77
2.4	Spatial Patterns in the $\text{Ni}/\text{H}_2\text{SO}_4$ Oscillator	84
2.5	Modeling the Spatiotemporal Patterns in Electrodissolution Processes	86
2.5.1	The Two-Dimensional Model for Bistable and Oscillatory Process	86
2.5.2	The Extension to Three-Dimensional Model	88
2.5.3	Modeling the Electrochemical Turbulence	98
2.6	Patterns in H_2 Oxidation	102
2.7	Patterns in CO Oxidation	108

2.8	Patterns in HCOOH Oxidation	110
2.9	Spatiotemporal Patterns in Sulfide Electrooxidation	122
2.10	Turing Patterns in Electrochemical Systems	123
2.11	Dendritic Patterns in Metal Electrodeposition	128
2.11.1	Dendritic Deposition on Solid Surfaces	128
2.11.2	Dendritic Deposition on Liquid/Liquid Interface	138
2.12	Dendritic Patterns in Silicon Electrodisolution	144
	References	147
3	Cooperative Dynamics of Coupled and Forced Oscillators	153
3.1	Coupled Oscillators	153
3.1.1	Outline Theoretical Aspects of Coupling the Electrochemical Oscillators	153
3.1.2	Single and Coupled H ₂ O ₂ Oscillators	156
3.1.3	Coupling in the Oscillatory Oxidation of Formic Acid	162
3.1.4	Coupled Fe/H ₂ SO ₄ Oscillators	164
3.1.5	Coupled Co/HCl + CrO ₃ Oscillators	170
3.1.6	Coupled Ni/H ₂ SO ₄ Oscillators	174
3.1.7	Coupled Oscillators and <i>IR</i> Compensation	182
3.1.8	Coupling the S-NDR Oscillators	184
3.1.9	Coupled Electrochemical Oscillators and Neural Cells	187
3.1.10	The Pitting Corrosion of Steel as a Cooperative Process	193
3.2	Forced Oscillators	204
3.2.1	The Perturbed Formaldehyde and Formic Acid Oscillators	204
3.2.2	The Forced Fe/H ₂ SO ₄ Oscillator	206
3.2.3	The Laser-Perturbed Fe/H ₂ SO ₄ Oscillator	209
3.2.4	The Forced Ni/H ₂ SO ₄ Oscillator	212
	References	216
4	Spatial and Spatiotemporal Patterns in Anodized Semiconductors	221
4.1	Spatiotemporal Nature of Silicon Electrooxidation and the Origin of Oscillations	221
4.1.1	The Model of Two Oxides	221
4.1.2	The Current-Burst Model	226
4.1.3	The Outline New Model Involving Ohmic Potential Drops	242
4.2	Self-organization in III–V Semiconductors	243
4.3	Anodization of Ti and the Patterned TiO ₂ Layers	248
4.3.1	Oscillations of Current During Anodization of Ti	248
4.3.2	TiO ₂ Nanotubes	249
4.3.3	TiO ₂ Nanogrooves	251
4.4	Overview of Spatiotemporal Self-organization in Etched Semiconductors	256
	References	260

5	Convection as a Source of Self-Organization in Electrochemical Systems	265
5.1	Convection as a Self-Organized Phenomenon	265
5.1.1	The Navier-Stokes Equation	265
5.1.2	Classical Bénard-Rayleigh Instability	266
5.2	Electrochemical Analogues of the Bénard-Rayleigh Instabilities	271
5.2.1	The $\text{Cu/CuSO}_4/\text{Cu}$ System	271
5.2.2	Oscillations in Electroformation of Ionic Liquids	276
5.3	Oscillatory Convective Instabilities Leading to Spatiotemporal Patterns	278
5.4	Bénard-Marangoni Instabilities	280
5.4.1	The Marangoni Number	280
5.4.2	Instabilities at the Mercury-Solution Interface	282
5.4.3	Instabilities at the Solid Electrode-Solution Interface	289
5.5	Bistability Caused by Potential-Dependent Convection	300
5.5.1	Experimental Realization	300
5.5.2	Linear Stability Analysis	300
5.6	Self-Induced Convection in the Processes at Hg Electrodes in Nonaqueous Media	307
5.7	The Old and New Versions of the Beating Mercury Heart	309
5.8	Convective Instabilities Caused by Gas Evolution Reactions in Electrode Processes	317
5.8.1	Oscillations in the Electrode Reactions of Anions at Solid Electrodes	317
5.8.2	Convection-Driven Oscillations in Methanol Oxidation	323
5.8.3	Convection-Driven Oscillations and Dendritic Formation During Metal Deposition	326
5.9	The Self-Organized Electrohydrodynamic Convection	332
5.9.1	Principles of the Electrohydrodynamic (EHD) Convection	332
5.9.2	EHD Convection in Liquid Crystals	336
5.9.3	EHD Convection in Colloidal Systems	338
5.9.4	The Low-Voltage EHD Convective Luminescent Patterns	344
5.9.5	Electroconvection in Membrane Systems	365
5.10	Interaction of Spatial Pattern Formation and Forced Convection	366
	References	368

6	Liquid Membrane and Other Membrane Oscillators	375
6.1	Dynamics of the Liquid-Liquid Interface and Liquid Membrane Systems	375
6.2	Liquid Membrane Systems as the Model Chemoreceptors	378
6.2.1	Construction and Oscillatory Dynamics of the Liquid Membrane System	378
6.2.2	Electrochemical Model of Taste Sensor	381
6.2.3	Electrochemical Model of Smell Sensor	385
6.3	Recent Developments in Liquid Membrane Oscillators	385
6.4	Outline Characteristics of Solid Membrane Oscillators	396
6.4.1	Biochemical Membrane Oscillators	396
6.4.2	Artificial Solid Membrane Oscillators	399
6.5	Oscillations in Conducting Polymer Systems	404
	References	406
7	Control of Electrochemical Chaos and Unstable Steady-States	411
7.1	Application of Map-Based Control Algorithms	411
7.2	Application of Derivative Control Strategy	413
7.3	Application of Delayed-Feedback Control	419
7.4	Application of Sinusoidal Forcing	423
7.5	Application of Sinusoidal Forcing to Control of Spatio-Temporal Behavior	425
7.6	Noise-Induced Order in Electrochemical Systems	431
7.7	Stabilization of Oscillations in the Systems with Spontaneous Drift	436
	References	438
	About the Author	441
	About the Editor	443
	Index	445