



---

# Contents

---

Preface.....	vii
Editor.....	ix
Contributors.....	xi
<b>1. Fundamentals of Corrosion.....</b>	<b>1</b>
<i>Hans-Henning Strehblow and Philippe Marcus</i>	
<b>2. Surface Effects on Hydrogen Entry into Metals.....</b>	<b>105</b>
<i>Elie Protopopoff and Philippe Marcus</i>	
<b>3. Anodic Dissolution.....</b>	<b>149</b>
<i>Michel Keddam</i>	
<b>4. Thin Oxide Film Formation on Metals.....</b>	<b>217</b>
<i>Francis P. Fehlner and Michael J. Graham</i>	
<b>5. Passivity of Metals.....</b>	<b>235</b>
<i>Hans-Henning Strehblow, Vincent Maurice, and Philippe Marcus</i>	
<b>6. Passivity of Austenitic Stainless Steels.....</b>	<b>327</b>
<i>Clive R. Clayton and Ingemar Olefjord</i>	
<b>7. Mechanisms of Pitting Corrosion.....</b>	<b>349</b>
<i>Hans-Henning Strehblow and Philippe Marcus</i>	
<b>8. Sulfur-Assisted Corrosion Mechanisms and the Role of Alloyed Elements.....</b>	<b>395</b>
<i>Philippe Marcus</i>	
<b>9. Further Insights on the Pitting Corrosion of Stainless Steels.....</b>	<b>419</b>
<i>Bernard Baroux</i>	
<b>10. Crevice Corrosion of Metallic Materials.....</b>	<b>449</b>
<i>Pierre Combrade</i>	
<b>11. Stress-Corrosion Cracking Mechanisms.....</b>	<b>499</b>
<i>Roger C. Newman</i>	
<b>12. Corrosion Fatigue Mechanisms in Metallic Materials.....</b>	<b>545</b>
<i>T. Magnin</i>	
<b>13. High-Temperature Corrosion.....</b>	<b>573</b>
<i>Michael Schütze</i>	

<b>14. Corrosion Prevention by Adsorbed Organic Monolayers and Ultrathin Plasma Polymer Films</b> .....	617
<i>Michael Rohwerder, Martin Stratmann, and Guido Grundmeier</i>	
<b>15. Atmospheric Corrosion</b> .....	669
<i>Christofer Leygraf</i>	
<b>16. Corrosion of Aluminum Alloys</b> .....	705
<i>Nick Birbilis, T.H. Muster, and Rudolph G. Buchheit</i>	
<b>17. Microbially Influenced Corrosion</b> .....	737
<i>Dominique Thierry and Wolfgang Sand</i>	
<b>18. Corrosion in Nuclear Systems: Environmentally Assisted Cracking in Light Water Reactors</b> .....	777
<i>F.P. Ford and P.L. Andresen</i>	
<b>19. Corrosion of Microelectronic and Magnetic Data-Storage Devices</b> .....	825
<i>Gerald S. Frankel and Jeffrey W. Braithwaite</i>	
<b>20. Organic Coatings</b> .....	863
<i>J.H.W. de Wit, D.H. van der Weijde, and G. Ferrari</i>	
<b>Index</b> .....	907





# 1

---

## *Fundamentals of Corrosion*

---

**Hans-Henning Strehblow**

*Ecole Nationale Supérieure de Chimie de Paris,*

*Centre National de la Recherche Scientifique*

and

*Heinrich Heine University Düsseldorf*

**Philippe Marcus**

*Ecole Nationale Supérieure de Chimie de Paris*

and

*Centre National de la Recherche Scientifique*

### CONTENTS

1.1	Introduction.....	2
1.2	Electrolytes and Solvents.....	3
1.3	Conductivity and Transfer Coefficient.....	5
1.4	The Structure of Electrolytes.....	6
1.4.1	XAS and Extended X-Ray Absorption Fine Structure (EXAFS) for Determination of the Short-Range Order.....	9
1.4.2	Short-Range Order of Dissolved Species.....	11
1.5	Debye–Hückel–Onsager Theory of Diluted Strong Electrolytes.....	13
1.5.1	Basic Discussion.....	13
1.5.2	Equivalent Conductivity of Strongly Dissociated Electrolytes.....	15
1.5.3	Equivalent Conductivity of Weakly Dissociated Electrolytes.....	18
1.5.4	Activity Coefficient.....	19
1.6	Some Basic Definitions in Electrochemistry.....	21
1.7	The Electrochemical Double Layer.....	23
1.8	Thermodynamics of Chemical Equilibria.....	30
1.8.1	Energy $U$ and Enthalpy $H$ .....	30
1.8.2	Entropy $S$ , Helmholtz Free Energy $F$ , Gibbs Free Energy or Free Enthalpy $G$ .....	33
1.8.3	Electrochemical Equilibrium and Nernst Equation.....	36
1.8.4	Potential–pH Diagrams.....	37
1.8.5	Reference Electrodes.....	41
1.9	Liquid Junction Potentials.....	42
1.10	Electrode Kinetics.....	43
1.10.1	Charge Transfer Overvoltage $\eta_{CT}$ and Butler–Volmer Equation.....	44
1.10.2	Diffusion Overvoltage $\eta_D$ .....	49
1.10.3	Ohmic Drop $\eta_\Omega$ and Microelectrodes.....	52

1.11	Electrochemical Methods .....	55
1.11.1	Electrochemical Cells .....	55
1.11.2	Potentiostatic Measurements .....	57
1.11.3	Galvanostatic Measurements .....	58
1.11.4	Rotating Disc Electrodes (RDEs) and Rotating Ring Disc Electrodes (RRDEs) .....	59
1.11.5	Electrochemical Transients .....	61
1.11.6	Impedance Spectroscopy .....	62
1.12	Reduction of Redox Systems .....	66
1.12.1	Hydrogen Evolution .....	67
1.12.2	Oxygen Reduction .....	70
1.13	Metal Dissolution .....	71
1.13.1	Basics of Metal Dissolution .....	71
1.13.2	High Rates of Metal Dissolution and Salt Precipitation .....	75
1.13.3	Selective Dissolution of Alloys .....	76
1.13.4	Metal Dissolution and Complex Formation .....	79
1.14	Metal Dissolution in Combination with Reduction Reactions .....	80
1.15	Heterogeneous Metal Surfaces and Local Elements .....	83
1.16	Protection .....	85
1.16.1	Cathodic Protection .....	85
1.16.2	Anodic Protection .....	87
1.16.3	Stray Currents .....	87
1.17	Inhibition of Corrosion .....	87
1.17.1	Inhibition by Adsorption .....	88
1.17.2	Inhibition by Precipitation of Compounds .....	91
1.17.3	Inhibition by Passivation .....	92
1.18	Semiconductor Electrochemistry and Photoelectrochemistry .....	93
1.18.1	Some Properties of Semiconductors .....	94
1.18.2	Electron Transfer at Semiconductor Electrodes .....	95
1.18.3	Photoelectrochemistry .....	99
1.19	Conclusion .....	102
1.20	Acknowledgments .....	102
	References .....	103























































































































