Lecture Notes in Engineering

Edited by C. A. Brebbia and S. A. Orszag

75

J. Deconinck

Current Distributions and Electrode Shape Changes in Electrochemical Systems



Springer-Verlag Berlin Heidelberg New York London Paris Tokyo Hong Kong Barcelona Budapest

CONTENTS.

NOMENCLATURE

CHAPTER 1. THE CURRENT DISTRIBUTION IN ELECTRO-CHEMICAL SYSTEMS

1.1. Introduction	1
1.2. The electrode-electrolyte interphase 1.2.1. The equilibrium situation 1.2.2. Electrode reactions 1.2.3. The activation overpotential η_a	2 2 4 6
1.3. Transport equations in dilute solutions1.3.1. The flux of a dissolved species1.3.2. The current density1.3.3. Conservation of mass1.3.4. The Poisson equation or electroneutrali-	9 11 11
ty 1.3.5. The continuity equation 1.3.6. The Navier-Stokes equation	12 13 13
1.4. Solution of the transport equations in dilute solutions 1.4.1. Basic system of equations 1.4.2. The potential model 1.4.3. The concentration overpotential η_c	14 14 17 20
1.5. The boundary conditions of the potential model 1.5.1. The boundary condition on the walls 1.5.2. The boundary conditions on the electrodes 1.5.3. Additional boundary conditions 1.5.3.1. Resistive electrodes 1.5.3.2. Resistance involved by coatings	22 22 23 27 27 27
1.6. Types of current distributions 1.6.1. Introduction 1.6.2. The primary distribution 1.6.3. The secondary distribution 1.6.4. The tertiary distribution 1.6.4.1. Distribution over microprofiles 1.6.4.2. Distribution over macroprofiles	30 30 31 33 35 36

1.7. The Wagner number	38
1.8. Electrode shape change 1.8.1. Faraday's law 1.8.2. The current efficiency 1.8.3. Moving boundaries and electrochemical machining 1.8.4. Equations to solve 1.8.5. Electrode shape change between parallel electrodes 1.8.6. Electrochemical machining between plane parallel electrodes	44 44 46 47 49 52
1.9. Conclusion	54
CHAPTER 2. SOLUTION OF THE POTENTIAL MODEL	
2.1. Introduction	56
2.2. Hypotheses and definitions	56
2.3. Weighted residual statements for the Laplace equation	58
2.4. Solution of current distributions with trial functions satisfying the field equations	63
2.5. Solution of current distributions with trial functions not satisfying the field equations 2.5.1. The finite difference method 2.5.2. The finite element method 2.5.3. The Newton-Raphson iteration associated with the finite element method 2.5.4. The method of straight lines	65 66 66 68
 2.6. Solution of current distributions based on weight functions satisfying the field equation 2.6.1. The boundary element method 2.6.2. The Newton-Raphson iteration process in boundary elements 	70 70 79
 2.7. The physical interpretation of the integral equation 2.7.1. The potential generated by a charged surface 2.7.2. The potential generated by a double source density on a surface 2.7.3. Green's formula and source distributions 	81 81 83 85

2.8. The outer normal convention.	86
2.9. Indirect and regular boundary methods	87
2.10. Comparison of the treated weighted residual methods	89
2.11. Solution of current distributions by electric simulation	91
2.12. Conclusion	92
CHAPTER 3. THE BOUNDARY ELEMENT METHOD TO SOLVE CURRENT DISTRIBUTIONS	
3.1. Introduction	94
 3.2. Concretization of the boundary element method 3.2.1. Choice of used elements 3.2.1.1. Two-dimensional problems 3.2.1.2. Three-dimensional axisymmetric problems 3.2.2. Combination of regions 	94 94 95 106 111
3.3. The overvoltage equations 3.3.1. The Butler-Volmer equation 3.3.2. The concentration overpotential 3.3.3. Linear and measured overpotentials	118 118 119 120
3.4. Solution of the non-linear system of equations 3.4.1. Solution of the linear system of equations 3.4.2. Iteration techniques for non-linear systems 3.4.2.1. The successive substitution method 3.4.2.2. The Newton-Raphson iteration method - Global convergence conditions 3.4.2.3. Convergence criteria 3.4.2.4. A Newton-Raphson iteration versus a successive substitution	120 120 121 121 122 124
3.5. Examples 3.5.1. The Hull-cell 3.5.2. The influence of overpotentials on singularities 3.5.3. Industrial production-type cells	130 130 133 138
3.5.3.1. Two-dimensional cell composed of an electrode with open part and separator 3.5.3.2. A chlorine production cell 3.5.4. Current distribution in a circular hole	138 141 143

3.6. Copper electrorefining: numerical and experimental results 3.6.1. Electrochemical data 3.6.1.1. The electrolytic solution 3.6.1.2. The overvoltages 3.6.2. The cell geometry 3.6.3. The measuring equipment 3.6.4. The experimental procedure 3.6.5. Experimental results 3.6.5.1. Measurement 1: 6 cm interelectrode distance 3.6.5.2. Measurement 2: 12 cm interelectrode distance 3.6.6. Comparison with calculations	146 146 146 148 149 152 154 154 155
3.7. Conclusion	162
CHAPTER 4. ELECTRODE SHAPE CHANGE	
4.1. Introduction	164
4.2. The discretization with respect to time 4.2.1. The Euler method 4.2.1.1. Convergence and accuracy 4.2.1.2. Stability 4.2.2. Higher-order integration schemes 4.2.2.1. The predictor-corrector method (Heun)	165 166 166 174 182 183
4.3. The electrode shape change algorithm 4.3.1. Electrodeposition	184 184
4.3.1.1. Electrode next to an insulator: internal angle > $\pi/2$	186
4.3.1.2. Electrode next to an insulator: internal angle $\leq \pi/2$ 4.3.2. Electrode dissolution 4.3.3. Electrochemical machining	188 189 190
4.4. Examples 4.4.1. Electrodeposition in a Hull-cell	191 191
4.4.2. Deposition and dissolution in a cell with sinusoidal profile	193
4.4.3. Anodic leveling and electrochemical machining in a cell with irregular shape 4.4.4. ECM in a cell with hemispherical cathode 4.4.5. Conclusion: comments on the efficiency of	196 199
the BEM	200
 4.5. Electrodeposition and electrode dissolution in copper electrorefining. Numerical and experimental results 4.5.1. Electrochemical data 	200 200

4.5.2. 4.5.3. 4.5.4.	The measuring equipment The experimental procedure	200 203 205
4.5.6.	calculations	20 <i>5</i> 21 <i>9</i>
4.6.	Conclusion	219
CHAPTE	ER 5. GENERAL CONCLUSION	221
REFERE	ENCES	224
APPENI	DICES	
A.1.1	Primary current distribution along a free cathode in parallel with an anode and perpendicular to an insulating boundary	243
A.1.2	Primary current distribution along an L-shaped cathode	247
A.1.3	Primary current distribution along a cathode being in line with an insulating boundary	251
A.2	Solution of the potential model using trial functions satisfying the field equation: example	255
A.3.1	Analytic integration of integrals involved by the two-dimensional boundary element method using straight elements	257
A.3.2	Evaluation of integrals involved by the boundary element method used to solve axisymmetric potential problems	267
A . 4	The global Newton convergence of the potential problem with non-linear boundary conditions	276