
Contents

1	Introduction and Research strategy	3
1.1	General context	3
1.2	Objectives and Research Strategy	6
2	Catalysis of proton transfer steps in proton-coupled electron transfer (PCET) reactions : experimental and numerical study	9
2.1	Introduction	9
2.1.1	Square scheme	10
2.1.2	Thermodynamic of the square-scheme	12
2.1.3	Kinetics of the square scheme	13
2.2	General acid-base catalysis and the Brönsted catalysis law	15
2.3	Experimental methods	19
2.3.1	Electrochemical techniques	19
2.3.2	Optical techniques	22
2.3.3	Materials and reagents	23
2.4	Model and numerical integrations	24
2.4.1	Model	24
2.4.2	Equations	25
2.4.3	Dimensionless equations	26
2.4.4	Dimensionless initial and boundary conditions	27
2.4.5	From equations to current values	29
2.4.6	Determination of parameters (D, v) to use in the numerical simulations	30
2.5	Numerical study	32
2.5.1	Comparison with non-catalyzed reactions	32
2.5.2	Influence of the chosen rate constants and scan rate combination .	35
2.5.3	Evolution of ΔE with the pH of the solution	39
2.6	Experimental study	40
2.6.1	Choice of the molecule	41
2.6.2	Electrode material	41

2.6.3 Electrochemical study of HPTS	42
2.6.4 Presentation of experimental peak potential <i>vs.</i> pH diagrams	43
2.6.5 Comparison between theoretical and experimental results	45
2.6.6 Optical properties of HPTS	47
2.7 Conclusions and perspectives	53
3 Spontaneous <i>vs.</i> natural convection in electrochemical systems	57
3.1 Introduction	57
3.1.1 Mass transport in electrochemistry	59
3.1.2 Theory of spontaneous convection	60
3.2 Turbulent form of the advection-diffusion equation	63
3.3 Numerical simulation: influence of the radial contribution	65
3.4 Introduction of fluctuations into the numerical simulations	67
3.5 Accounting for natural convection	69
3.6 Comparison with experiments	70
3.7 General comments and conclusion	73
4 Natural convection during PCET reactions	75
4.1 Introduction	75
4.2 Model	79
4.2.1 Dimensional equations	79
4.2.2 Dimensionless equations	80
4.2.3 Boundary conditions	81
4.2.4 Verification of numerical simulations	83
4.2.5 Determination of the Schmidt number value	84
4.3 Horizontal and vertical density gradients	85
4.4 Short-time evolution of natural convection	86
4.4.1 Influence of the solutal expansion coefficients	86
4.4.2 Influence of coupled reactions	88
4.4.3 Influence of rate constants on natural convection	91
4.4.4 Influence of chosen pK_{as}	92
4.5 Evolution of the velocity along a double potential step	93
4.6 Long time evolution	94
4.6.1 Relation between concentration profiles and current measurement	97
4.6.2 Density profiles	100
4.6.3 Influence of the electrode radius and experimental times on the dynamics	102
4.6.4 Evolution of the convective roll in z -direction with time	106
4.6.5 Influence of the insulating shell around the electrode	107
4.7 Conclusions and perspectives	109

5 Impact of Marangoni flows on the electrochemical conversion A → B	111
5.1 Introduction	111
5.1.1 Marangoni flows in chemical and electrochemical systems	112
5.2 Model and numerical simulations	114
5.3 Study of the impact of Marangoni flows alone	117
5.3.1 Surface tension profiles	117
5.3.2 Velocity evolution	118
5.4 Study of the impact of Marangoni flows coupled to buoyancy-driven convection	119
5.4.1 Case 1: product less dense and more surface active than the reactant	120
5.4.2 Case 2: product less dense and less surface active than the reactant	121
5.4.3 Case 3: product denser and more surface active than the reactant	122
5.4.4 Case 4: product denser and less surface active than the reactant .	123
5.4.5 Velocity evolution: comparison between the four cases	124
5.4.6 Relation with the current	127
5.5 Relationship between density and surface tension	127
5.5.1 Along an electrochemical reaction	128
5.6 Conclusion and perspectives	130
6 Conclusions and prospects	131
Bibliography	137