

Kinetic Oscillations and Spatiotemporal Self-Organization in Electrocatalytic Reactions

Experimental Analysis, Modeling and Classification

Dissertation

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Klaus-Peter Strasser

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Committee in charge:

Prof. Dr. G. Ertl, Fritz-Haber-Institut der Max-Planck-Gesellschaft

Prof. Dr. H. Baumgärtel, Freie Universität Berlin, Fachbereich Chemie

Date of thesis defense:

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Preface

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Publications

1. Strasser, P.; Stemwedel, J. and Ross, J., **Analysis of a chemical reaction mechanism**, *J.Phys.Chem.*, 97,2851(1993)
2. Alessio, R.; Belli-Dell'Amico, D.; Calderazzo, F.; Englert, U.; Guarini, A.; Labella, L. and Strasser, P., **N,N-Dialkylcarbamato Complexes of the d10 cations of Copper, Silver and Gold**, *Helv.Chim.Acta.*, 81,219(1998)
3. Strasser, P.; **Raumzeitliche Strukturbildung in enzymatischen Kinetiken**, Diplomarbeit, Universität Tübingen, 1995
4. Baier, G.; Strasser, P. and Kummer, U.; **Instabilities in a simple enzyme reaction caused by pH-dependence**, *Z. Naturforsch.*, 50a,1147(1995)
5. Strasser, P.; Rössler, O.E. and Baier, G.; **Hyperchaos and chemical turbulences in enzymatic reaction-diffusion kinetics**, *J.Chem.Phys.*, 104,9974(1996)
6. Eiswirth, M.; Bürger, J.; Strasser, P. and Ertl, G., **Oscillating Langmuir Hinshelwood Mechanisms**, *J.Phys.Chem.*, 100,19118,(1996)
7. Strasser, P.; Lübke, M.; Raspel, F.; Eiswirth, M. and Ertl, G., **Oscillatory instabilities during formic acid oxidation on Pt(100), Pt(110) and Pt(111) under potentiostatic control, I.Experimental**, *J.Chem.Phys.*, 107,979(1997)
8. Strasser, P.; Eiswirth, M. and Ertl, G., **Oscillatory instabilities during formic acid oxidation on Pt(100), Pt(110) and Pt(111) under potentiostatic control, II. Model calculations**, *J.Chem.Phys.*, 107,991(1997)
9. Strasser, P.; Lübke, M.; Parmananda, P.; Eiswirth, M. and Ertl, G., **Mechanistic analysis using derivative feedback control techniques**, *J.Phys.Chem.B*, 102,3227(1998)
10. Strasser, P. and Ata, M., **Electrochemical synthesis of lithium-doped, polymerized C₆₀**, *J.Phys.Chem.B*, 102,4131(1998)
11. Strasser, P.; Lübke, M.; Eickes, C. and Eiswirth, M., **Modeling galvanostatic potential oscillations in the electrocatalytic iodate reduction system**, *J.Electroanal.Chem.*, 462,19(1999)
12. Christoph, J.; Strasser, P.; Eiswirth, M. and Ertl, G., **Remote Triggering of Waves in an Electrochemical System**, *Science*, 284,291(1999)

In references 7-9 and 11,12 parts of the present thesis have been published.

Curriculum Vitae

DOB 04/18/1969

Education

- since 6/95 **Fritz-Haber-Institut der Max-Planck-Gesellschaft:**
Phd-degree in Physical Chemistry
- 11/93 - 3/95 **Tübingen University:**
'Diplom'-degree in chemistry
Nonlinear Enzyme Kinetics (**Prof. O.E. Rössler**)
- 10/92 - 10/93 **Pisa University:**
Research assistantship
Coordinative Chemistry, Homogeneous Catalysis (**Prof.F. Calderazzo**)
- 7/91 - 10/92 **Stanford University:**
Research assistantship
Instabilities, Oscillations in chemical reaction systems (**Prof. J. Ross**)
- 10/88 **Tübingen University:**
Chemistry 'Diplom'-program
- 1979 - 1988 Middle and High School at Heilbronn

Internships, work experience

- 08/98 - 10/98 **Andersen Consulting, Strategic Services**
Strategic management consulting
- 10/97 - 12/97 **Sony Corporation Research Center, Yokohama**
Materials Science Division, Fullerene Electrochemistry
- 7/96 - 10/96 **Sony Corporation Research Center, Yokohama**
Material Science Division

Summer schools

- 5/96 **Nonlinear Dynamics in Medicine and Biology,**
Center for Nonlinear Dynamics, McGill University, Montreal
Prof. Glass
- 8/95 **Surface chemistry and catalysis:**
Heyrovsky Institute, Prague, Prof. Schwartz
- 9/94 **Theory of complex dynamical systems in chemistry,**
Olang, Italy Prof. Müller, Dr. Eiswirth

