

Non-equilibrium growth patterns and oscillations during electrochemical deposition of Zn-Cu binary system in batch and flow reactors

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Abstract : Growth patterns of Zn-Cu alloys in the η and β phases have been developed and examined. Patterns become more compact and dense on increasing the copper content and field intensity. The compactness is more in the β phase than those in the η phase. Fractal dimension D was computed in each case by box counting method. Weight of aggregates at different concentrations of CuSO_4 was determined. Electrodeposited aggregates were characterized by X-ray diffraction (XRD) study. Electrodeposition of metals under the diffusion limited conditions shows spontaneous potential oscillations. Cathode potential was measured as a function of time during electrochemical deposition of Zn, Cu and Zn-Cu alloys in batch and in a Continuously Stirred Tank Reactors (CSTR). The morphology, amplitude and frequency of oscillation were found to depend on the copper content. A transition from biperiodicity to periodic oscillation was observed when copper sulphate was introduced in ZnSO_4 solution.

Keywords : Electrochemical deposition, growth patterns, electrochemical oscillation, batch and flow reactors, Zn-Cu binary system.

Introduction

There is considerable interest in the interfacial pattern formation during electrodeposition and crystal growth, which have relevance to biological systems. A renewed interest in electrochemical pattern formation has been seen in the past few years¹⁻⁸. It is well recognized that electrodeposition is a typical example of far from equilibrium growth phenomena^{9,10}. On imposing external constraints like constant potential drop between two electrodes far from equilibrium situation is created. Non-equilibrium growth phenomenon has been widely recognized from both, basic and applied point of view^{11,12}. Electrodeposition of different metals such as zinc^{1,13-16}, copper¹⁷⁻²², lead²³ gives rise to aggregates with complex shapes including fractals. The branched fractal structures formed by non-equilibrium electrodeposition of metals have been considered as model systems for the study of branching and fractal growth processes²⁴. Five different intermetallic phases of Cu-Zn system exist namely β , π , γ , ϵ and η phases which differ in Zn composition. η phase is the random substitutional solution of Cu in Zn with 97-100%

Zn composition while β is an intermetallic compound of approximate stoichiometry Cu-Zn (40-50% Zn). Previous experiments on fractal metallic electrodeposition have been focused mainly on one component system^{14,15,25,26}. However, a very little work has been reported on morphological studies of binary systems^{5,27,28}. Zinc based alloys are widely used as corrosion protective coatings for steel. Electrochemical deposits from a mixed aqueous solutions of Zn and Cu in a batch reactor was examined by Eba *et al.*⁵ and the morphologies were examined by optical and scanning electron microscope.

Oscillatory electrodeposition²⁹ is an interesting phenomena from the point of view of production of micro/nanostructured materials^{2,3,5,6,12,13,30}. Most of the studies are limited to the oscillatory deposition^{12,23,31,32} and dissolution^{33,34} of single metals. However, a few results on the oscillatory electrochemical deposition of binary systems are reported in a batch reactor only^{27,28}.

In the present paper we report electrodeposition and growth behaviour of the deposits obtained from aqueous solutions of ZnSO_4 , CuSO_4 and ZnSO_4 containing CuSO_4

in different proportions at different field intensities, determination of fractal dimension of electrodeposits, XRD and thermal studies, cathode potential changes with time during the electrodeposition of Zn, Cu and Zn-Cu intermetallic alloy in η and β phases in batch and flow reactors.

Experimental

Zinc sulphate (Qualigens, LR), cupric sulphate (BDH, AR) were used as such. The electrolyte solutions were prepared with reagent grade chemicals in doubly distilled water.

Electrodeposition of metals and growth kinetics in a batch reactor : The electrodeposition of metals was carried out in a batch reactor using an experimental setup shown in Fig. 1. The experiment was conducted in a petridish containing 30 ml of electrolyte solution. The electrolyte used in the present study was an aqueous solution of zinc sulphate (0.1 M), copper sulphate (0.1 M) and their mixtures. Concentrations were in the range

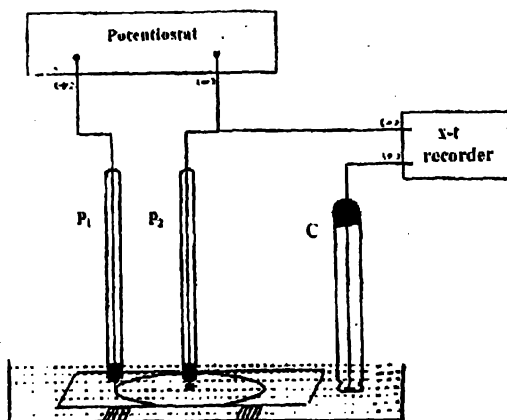


Fig. 1. Experimental setup for electrodeposition of metals. P_1 = circular platinum anode, P_2 = vertical platinum cathode. Radius of circular platinum anode = 2.5 cm. C = Calomel electrode.

3.3×10^{-4} to 2.28×10^{-3} M CuSO_4 and 9.77×10^{-2} to 9.97×10^{-2} M ZnSO_4 . A glass slide was put in the dish containing solutions of above two spacers in such a manner that small volume of the solution (thickness ~ 1 mm) was just above the slide. A circular platinum anode (P_1) and a vertical platinum cathode (P_2) were put into the solution. The diameter of the platinum wire was 0.34

mm, while the inner diameter of the circular platinum anode was 25 mm. The circular anode was placed above the slide and cathode was put in the center of the circular anode just touching the solution surface. Deposition started at the cathode (at air/liquid interface) by applying a dc voltage under potentiostatic conditions. The thickness of the deposited aggregate was ~ 0.08 mm. Potential was varied in the range 2.0–2.8 V/cm. No gas evolved was observed during deposition. A calomel electrode was inserted in the solution and attached with a x-t recorder to monitor potential changes during electrodeposition of metals. The entire experiment was performed at room temperature. Different types of growth morphologies were obtained. Microphotographs were taken with a KODAK Digital camera. Electrodeposited growth morphologies are shown in Fig. 2. Kinetics of electrodeposition was studied by recording the weight of the deposited mass as a function of Cu content in the solution. Results are shown in Fig. 3.

Powder X-ray diffraction studies : Powder X-ray diffraction patterns of electrodeposited aggregates were taken to compare the results of intermetallic η phase material with those of the individual metal aggregates. Results are shown in Fig. 4.

Cathode potential changes with time during electrochemical deposition in a batch reactor :

The experimental setup of a batch reactor shown in Fig. 1 was employed to monitor the potential changes at the cathode during electrochemical deposition of individual metals and the binary system at an air/water interface. Results are shown in Fig. 5. Optical density of an aqueous solution containing ZnSO_4 and CuSO_4 (Zn 50.0%, Cu 50.0%) was measured before and after electrochemical deposition at $\lambda_{\text{max}} = 804$ nm and found to be reduced after electrochemical deposition due to consumption of Cu^{2+} . Therefore, it was required to perform the experiment in CSTR to maintain the system far from equilibrium for a longer duration and to maintain the concentration constant.

Electrochemical deposition experiments in a CSTR : In order to maintain the electrolyte concentration con-

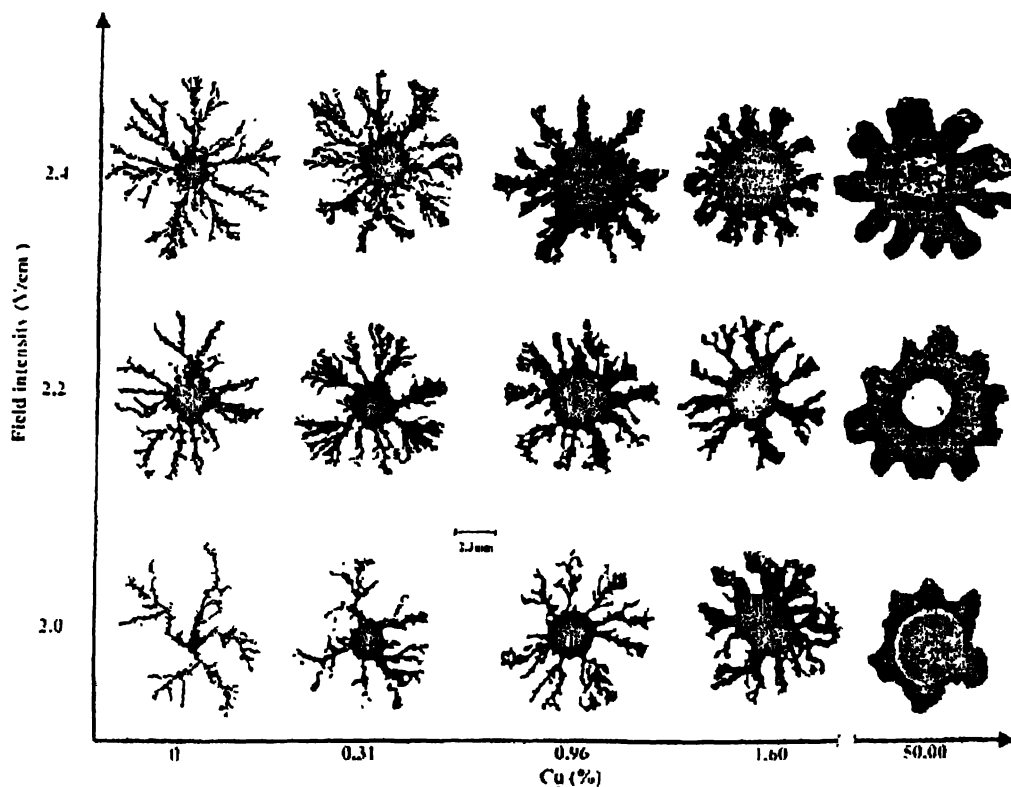


Fig. 2. Microphotographs of electrodeposited aggregates obtained from aqueous solutions of $ZnSO_4$ and $ZnSO_4$ containing $CuSO_4$ in different proportions and field intensities in the range 2.0–2.4 V/cm.

stant throughout the experiment, a Continuously Stirred Tank Reactor (CSTR) was used as shown in Fig. 6. It consists of a flat bottom petri dish having an outlet nozzle (O) at the corner. A glass slide was put in the dish above the two spacers in such a manner that only a small volume of the electrolyte solution (thickness ~ 1 mm) was just above the slide. The electrolyte used in the present study was an aqueous solution of zinc sulphate ($0.1 M$), copper sulphate ($0.1 M$) and their mixtures. Concentrations were in the range 3.3×10^{-4} to $2.28 \times 10^{-3} M$ $CuSO_4$ and 9.77×10^{-2} to $9.97 \times 10^{-2} M$ $ZnSO_4$. The level of the solution in the petri dish was maintained constant with help of a reservoir (B). Electrolyte solution was influxed at a flow rate of 2 ml/min. Remaining part of the experimental setup was the same as described in case of the batch reactor. In case of CSTR, optical den-

sity of $ZnSO_4$ - $CuSO_4$ solution was found to be constant before and after electrodeposition. Results are shown in Fig. 7.

Results and discussion

We have developed different intermetallic phases of zinc and copper from their aqueous solutions under different experimental conditions by varying copper content and field intensity under potentiostatic condition, employing the experimental setup shown in Fig. 1. Circular platinum anode and vertical platinum wire cathode were employed. The deposit resulting from electrochemical deposition experiment is generated by the cathodic reduction of a metal ion,



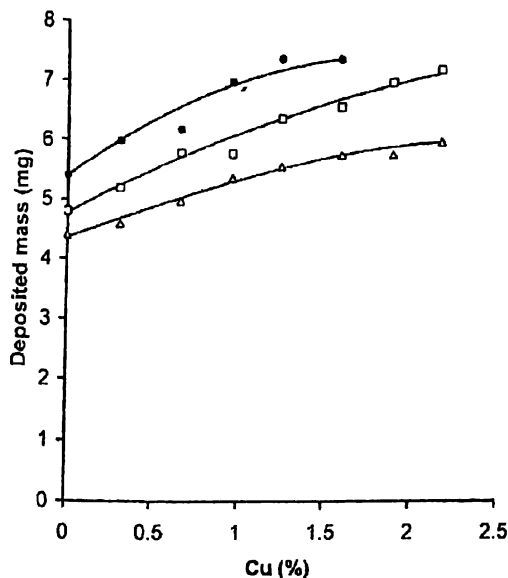


Fig. 3. Dependence of mass of electrodeposited aggregate on copper content in $\text{ZnSO}_4\text{-CuSO}_4$ solution in η phase. Conditions: $[\text{ZnSO}_4] = 0.1 \text{ M}$, field intensities (□) 2 V/cm, (Δ) 2.2 V/cm and (●) 2.4 V/cm.

where the transport of the cation is due to its migration in the presence of electric field. Growth was started immediately after applying the electric field. The patterns adopt various irregular fractal shapes with different fractal dimensions. Fractal growth patterns are shown in Fig. 2. The fractal dimension D of the scanned patterns were calculated by box counting method using the relation $N \sim r^D$. Results show that the patterns become more compact and dense on increasing (i) copper content in the aggregate and (ii) field intensity. The compactness is more in the β phase (high copper content) than those in the η phase (low copper content).

The dynamics of growth of different intermetallic phases of copper and zinc was studied under different conditions of copper content and field intensity. It was followed by measuring the weight of the electrodeposited aggregates of different composition corresponding to η phase. It varies non linearly as shown in Fig. 3. In case of β phase (50% Zn and 50% Cu), the dependence of weight of aggregates (w) varies linearly with field intensity (V). It obeys the relation $w = mV + c$ where m and

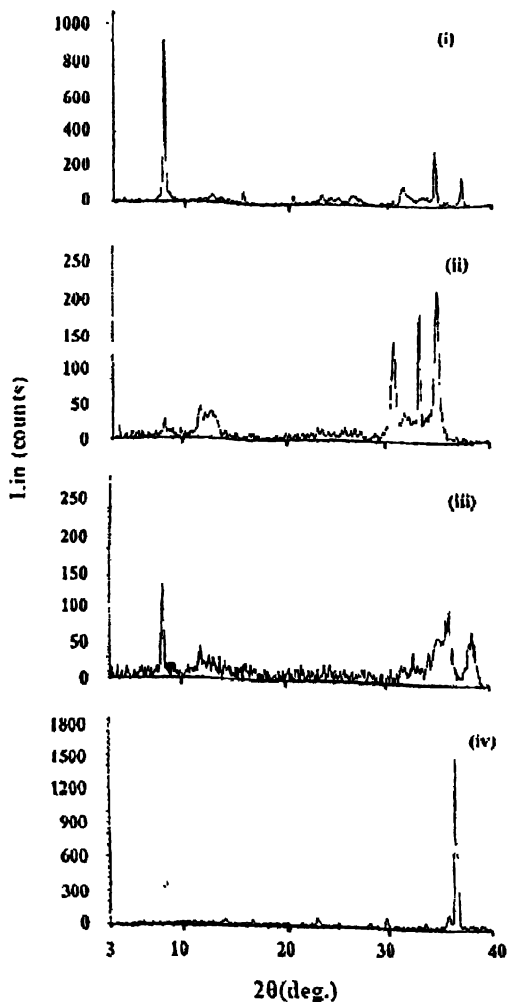


Fig. 4. XRD patterns of electrodeposited aggregates obtained from (i) ZnSO_4 , (ii-iii) ZnSO_4 containing CuSO_4 in various compositions (Zn 98.40%, Cu 1.60% and Zn 50%, Cu 50%) and (iv) CuSO_4 .

c are slope and intercept respectively. The value of correlation coefficient was 0.99. Crystal structures of Zn and intermetallic η phase are quite different as evident by XRD studies. XRD results (Fig. 4) show that characteristic lines for Zn, Cu, η and β phases are different.

Far from equilibrium phenomena including temporal oscillations are of considerable interest in chemical dynamics. Electrodeposition of some metals under far equilibrium conditions give rise to nonlinear electrochemical

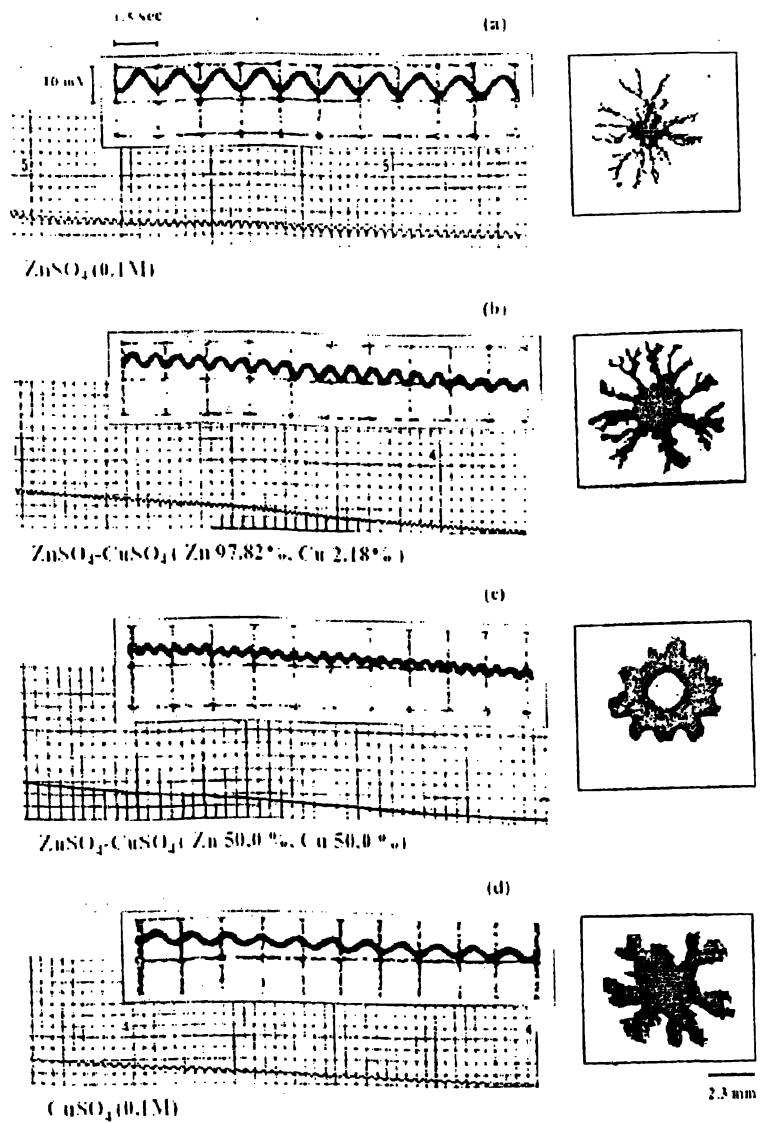


Fig. 5. Cathode potential changes with time during electrodeposition in batch reactor from aqueous solutions of (a) $ZnSO_4$, (b-c) $ZnSO_4$ containing $CuSO_4$ in different compositions (Zn 97.82%, Cu 2.18% and Zn 50%, Cu 50%) and (d) $CuSO_4$.

oscillations. Cathode potential changes with time during the process of electrodeposition of Zn, Cu and their intermetallic η and β phases have been studied under potentiostatic condition in batch and flow reactors. During the process of electrodeposition different morpholo-

gies and oscillations of the electrode potential are observed. Results of the batch reactor experiments are shown in Fig. 5. Amplified views are shown in the inset of each trace alongwith the corresponding morphologies. Amplitude of oscillation and frequency depend on the composi-

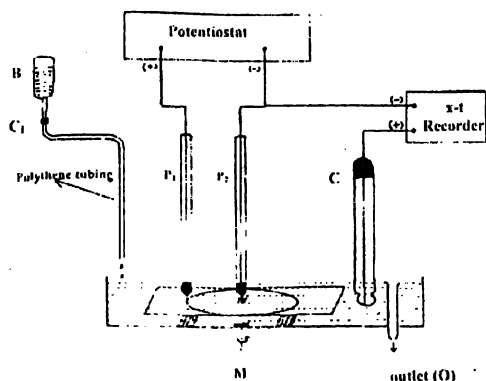


Fig. 6. Experimental setup of Continuously Stirred Tank Reactor to monitor potential changes with time. P_1 = circular platinum anode, P_2 = vertical platinum cathode, B = reservoir, C = calomel electrode, C_1 = control knob, M = magnetic stirrer.

tion of electrolyte used. Addition of CuSO_4 in ZnSO_4 reduced the amplitude and increased the frequency of oscillation (Fig. 5). Amplitude is minimum in the β phase. The morphologies of zinc and copper are shown in Figs. 5a and d. On addition of copper sulphate in the zinc sulphate solution, compactness is increased (Figs. 5b and c), amplitude of oscillation is decreased and frequency of oscillation increased on increasing the copper content. In order to maintain the electrolyte concentration constant throughout, experiments were also performed in a CSTR (Fig. 6). Electrolyte solutions (ZnSO_4 , CuSO_4 and ZnSO_4 containing CuSO_4) were influxed at a fixed flow rate of 2 ml/min. Such an arrangement permitted maintenance of constant concentration around the electrode. It was ensured by measuring the optical density of CuSO_4 - ZnSO_4

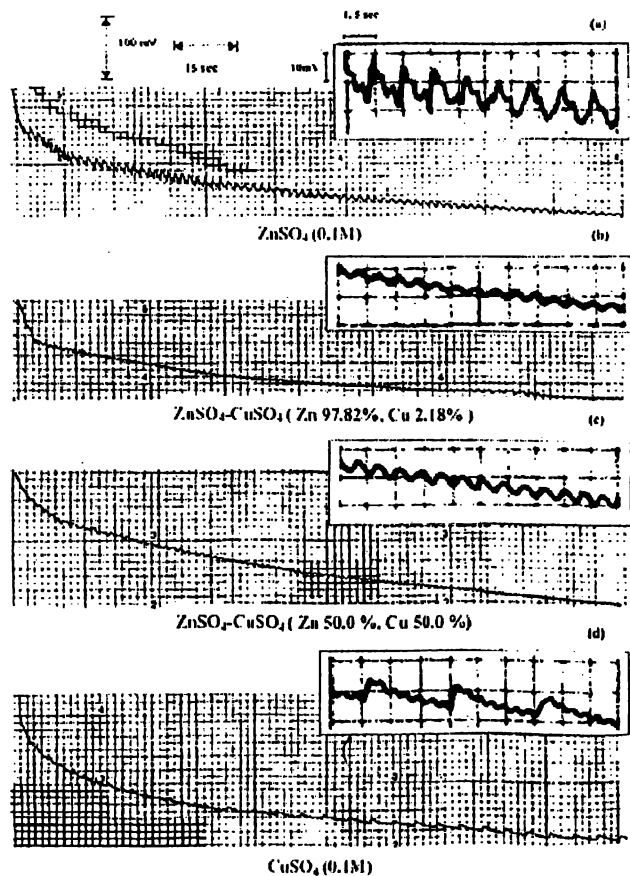


Fig. 7. Cathode potential changes with time during electrodeposition in CSTR from aqueous solutions of (a) ZnSO_4 , (b-c) ZnSO_4 containing CuSO_4 in different compositions (Zn 97.82%, Cu 2.18% and Zn 50%, Cu 50%) and (d) CuSO_4 .

solution before and after electrodeposition. Results obtained for electrodeposition of Cu, Zn and intermetallic η and β phases in CSTR are shown in Fig. 7. It was found that (i) cathode potential decreased with time in each case, (ii) biperiodicity and multiple periodicity were observed in case of zinc and copper electrodepositions respectively (Figs. 7a and d) and (iii) there is a transition from biperiodicity to periodic oscillation when copper sulphate was introduced in the zinc sulphate solution corresponding to η and β phases (Figs. 7b and c).

Conclusion :

Experiments on electrodeposited growth patterns of zinc, copper and zinc based alloys under different conditions lead to the formation of irregular fractal shapes with varying fractal dimension. From these experiments we conclude that the patterns become more compact and dense on increasing copper content and field intensity. The compactness is more in the β phase than those in the η phase. The dependence of weight of aggregates varies non linearly in η phase. In case of β phase the dependence of weight of aggregates varies linearly with field intensity. XRD studies showed that Zn, Cu, η and β phases are different. Cathode potential was monitored as a function of time during electrodeposition in batch and flow reactors. Amplitude of oscillation and frequency both depend on the composition of electrolyte used. In case of batch reactor experiment, on addition of copper sulphate in zinc sulphate solution, compactness and frequency of oscillation were increased, while amplitude of oscillation is decreased. Amplitude is minimum in the β phase. In case of CSTR, cathode potential decreased with time in each case, biperiodicity and multiple periodicity were observed in case of Zn and Cu electrodeposition respectively, while the oscillation is periodic in η and β phases.

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References

1. S. Nakanishi, T. Nagai, K. Fukami, K. Sonoda, N. Oka, D.

- Ihara and Y. Nakato, *Langmuir*, 2008, **24**, 2564.
2. S. Nakanishi, S. Sakai, K. Nishimura and Y. Nakato, *J. Phys. Chem. (B)*, 2005, **109**, 18846.
 3. J. Christoph and M. Eiswirth, *Chaos*, 2002, **12**, 215.
 4. S. Nakanishi, K. Fukami, T. Tada and Y. Nakato, *J. Am. Chem. Soc.*, 2004, **126**, 9556.
 5. H. Eba and K. Sakurai, *J. Electroanal. Chem.*, 2004, **571**, 149.
 6. S. Nakanishi, K. Fukami, T. Tada and Y. Nakato, *J. Am. Chem. Soc.*, 2004, **126**, 9556.
 7. Z. Fei, R. G. Kelly and J. L. Hudson, *J. Phys. Chem.*, 1996, **100**, 18986.
 8. G. Ertl, *Science*, 1991, **254**, 1750.
 9. L. M. Sander, "The Physics of Structure Formation", eds. W. Guttinger and G. Dangelmayr, Springer, Berlin, 1987, 257.
 10. D. A. Kessler, J. Koplic and H. Levine, *Adv. Phys.*, 1988, **37**, 255.
 11. F. Sagues, F. Mas, M. Vilarrasa and J. M. Costa, *J. Electroanal. Chem.*, 1990, **278**, 351.
 12. S. Bodea, L. Vignon, R. Ballon and P. Molho, *Phys. Rev. Lett.*, 1999, **83**, 2612.
 13. F. Argoul, J. Huth, P. Merzeau, A. Ameodo and H. L. Swinney, *Physica D*, 1993, **62**, 170.
 14. M. Matsushita, M. Sano, Y. Hayakawa, H. Honjo and Y. Sawada, *Phys. Rev. Lett.*, 1984, **53**, 286.
 15. M. Matsushita, Y. Hayakawa and Y. Sawada, *Phys. Rev. (A)*, 1985, **32**, 3814.
 16. Y. Sawada, A. Dougherty and J. P. Gollub, *Phys. Rev. Lett.*, 1986, **56**, 1260.
 17. R. M. Brady and R. C. Ball, *Nature (London)*, 1984, **309**, 225.
 18. D. B. Hibbert and J. R. Melrose, *Phys. Rev. (A)*, 1988, **38**, 1036.
 19. J. M. Costa, F. Sagues and M. Vilarrasa, *Phys. Rev. (A)*, 1991, **43**, 7057.
 20. D. Barkey, F. Oberholtzer and Q. Wu, *Phys. Rev. Lett.*, 1995, **75**, 2980.
 21. C. Leger, J. Elezgaray and F. Argoul, *Phys. Rev. (E)*, 2000, **61**, 5452.
 22. S. Zhong, Y. Wang, M. Wang, M. Zhang, X. Yin, R. Peng and N. Ming, *Phys. Rev. (E)*, 2003, **67**, 061601.
 23. R. P. Rastogi, I. Das, A. Pushkarna and S. Chand, *J. Phys. Chem.*, 1993, **97**, 4871.
 24. V. Fleury, *Nature*, 1997, **390**, 145.
 25. D. Grier, E. Ben-Jacob, R. Clarke and L. M. Sander, *Phys. Rev. Lett.*, 1986, **56**, 1264.
 26. F. Argoul, A. Arneodo, J. Elezgaray, G. Grassean and H. L. Swinney, *Phys. Rev. Lett.*, 1988, **61**, 2558.
 27. I. Das and S. S. Mishra, *Indian J. Chem., Sect. A*,

- 2000, 39, 1005.
28. A. Milchev, E. Michailova, R. Lacmann and B. Muller-Zulow, *Electrochimica Acta*, 1993, 38, 535.
 29. D. L. Piron, I. Nagatsugawa and C. Fan, *J. Electrochem. Soc.*, 1991, 138, 3296.
 30. A. Survila, Z. Mochus and R. Juskenas, *Electrochimica Acta*, 1998, 43, 909.
 31. K. Fukami, S. Nakanishi, H. Yamasaki, T. Tada, K. Sonoda, N. Kamikawa, N. Tsuji, H. Sakaguchi and Y. Nakato, *J. Phys. Chem. (C)*, 2007, 111, 1150.
 32. K. Fukami, S. Nakanishi, Y. Sawai, K. Sonoda, K. Murakoshi and Y. Nakato, *J. Phys. Chem. (C)*, 2007, 111, 3216.
 33. O. Lev, M. Sheintuch, L. M. Pisemen and Ch. Yarnitzky, *Nature*, 1988, 336, 458.
 34. J. L. Hudson and J. Tabora, *Phys. Lett. (A)*, 1993, 179, 355.