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Copper Fractal Growth Pattern in Polymer Systems

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Abstract

This paper presents the effect of polymer (polyvinyl alcohol) on the growth of copper fractal formation. A thin layer electrochemical cell was designed for the study of copper electrodeposition process. The structure and morphology for the copper fractal patterns were investigated by scanning electron microscopy (SEM). The copper fractal dimension was measured by using box counting method. On the basis of diffusion limited aggregation (DLA) model, growth pattern of copper fractal is two dimensional in nature. The copper fractal dimension is affected by the composition of polyvinyl alcohol. The growth pattern of copper fractal formation was measured under constant potential condition.

Keywords: fractal, copper, SEM, polyvinyl alcohol

1. Introduction

Polymers are usually preferred for the processing and fabrication of devices because of flexibility, stability, strength, light-weighting and bio-degradability (Kato et al., 2004; Hatamie, Dhole, Ding, & Kale, 2009; Ahmad, Deepa, Sen, Kazim, & Agarwal, 2011). Polyvinyl alcohol (PVOH) is a water-soluble synthetic polymer. It is resistant to oil, grease and some solvents. These properties are useful in such areas as membrane, textile sizing and finishing, adhesive, coatings and paints (Saeed, Masood, & Uddin, 2008).

The word fractal indicates mathematical entities having self similarity at different length scales. Fractal geometry is very useful in natural sciences, including chemistry, physics, biology, meteorology, geology as well as in engineering research mainly in material science (Zhou, He, & Guo, 1999). In nature examples of vascular systems, snowflakes, ferns, mountains, clouds, lightning and river networks showing fractal pattern (Teixidor, Park, Mukherjee, Kang, & Madou, 2009).

Diffusion and aggregation usually dominates the transport process as in ion deposition, electrodeposition and in other solidification processes. The diffusion limited aggregation (DLA) model provides a basis for fractal growth pattern or geometry (Nittmann & Stanley, 1986; 1987; Chen & Wilkinson, 1985). This fractal geometry in electrochemical cells increases the electrochemically active surface area by decreasing the transport energy lost inside the network.

Andreoli et al. (2011) studied the electrodeposition of hierarchical micro/nanostructures of copper hyroxysulfates on thin film of polypyrrole-polystyrene sulfonate. Some researchers have reported the work of copper fractal on polypyrrole doped with different anions (Sakar, Zhou, Tannous, & Leung, 2003; Cioffi et al., 2001). Akbar et al. (2009) reported that the fractal growth pattern of zinc dendrites was affected by different experimental conditions and the value of fractal dimension was estimated as 1.669. Murugan et al. (2012) studied the fractal patterns formation in polyacrylic acid systems in films due to the aggregation of inter-polymer adducts driven by hydrogen bonding and other non-covalent interactions. Qi et al. (2001) observed the defect-free growth of $BaSO_4$ nanofilaments in aqueous polymer solutions based on amorphous precursor particles. It was used to produce bundles or cones of highly anisotropic $BaSO_4$ nanofilaments by slow transformation. In the past few years, metal fractal structures including metal-polymer composites have attracted much attraction on the basis of their significance (Ji, Li, Liu, Hu, & Liu, 2008; Amir, Ali, & Mohamed, 2011).

Copper fractal growth patterns were studied in aqueous and in aqueous polyvinyl alcohol systems ranging from 0.1 to 1.0 $g{\cdot}dL^{-1}$ at a constant potential of 10 V. The purpose of this study is to investigate the effect of polymer (polyvinyl alcohol) addition on the fractal geometry and pattern. The growth pattern of copper fractal with the variation in polyvinyl alcohol composition was evaluated and the results are explained in terms of structural divergence.

2. Experiment

All the glassware of Pyrex A grade quality were used. Double distilled water having conductivity 0.06 μS.cm^{-1} was used for experimental purpose. Polyvinyl alcohol (PVOH) of E. Merck, (< 98% hydrolyzed), having average molecular weight 65075.11 Da. Copper sulphate pentahydrate ($CuSO_4.5H_2O$) of E. Merck, 99% pure, were used without further purification.

Stock solution of PVOH was prepared by dissolving required amount of PVOH in double distilled water at 353 ± 0.1 K. Different compositions of aqueous PVOH systems (0.1, 0.3, 0.5 and 0.7 g·dL^{-1}) were prepared from the stock solution of 1.0 g·dL^{-1} by dilution of stock solution. Copper sulphate of 0.2 mol.dm^{-3} solution was prepared by dissolving the required amount in aqueous and in different compositions of aqueous PVOH.

Experiments were carried out by using thin layer electrochemical cell. It was prepared by using two plastic sheets of few millimeters in thickness. One for making base of the thin layer cell which is white in color and a transparent sheet was used to cover the cell. Copper metallic ring was used as an anode, diameter and thickness of ring was 2.40 mm and 2 mm respectively. The thickness of ring separated the two layers from each other. A hole in the centre of cover was made to insert cathode (carbon rod) of 4.10 mm diameter. First metallic copper ring was placed on the base sheet; subsequently specific volume of solution was poured into the ring. The whole assembly was covered with caution to prevent the air bubbles formation in the solution. Electrical circuit for fractal formation comprised of an AC-DC adapter of 1.5 to 12 V having output of DC 1.5 to 12 V, digital multimeter rating 200 mA, digital ammeter and potientiometer upto 1.0 KΩ rating 0.5 mA. The complete setup of designed thin layer cell is shown in Figure 1.

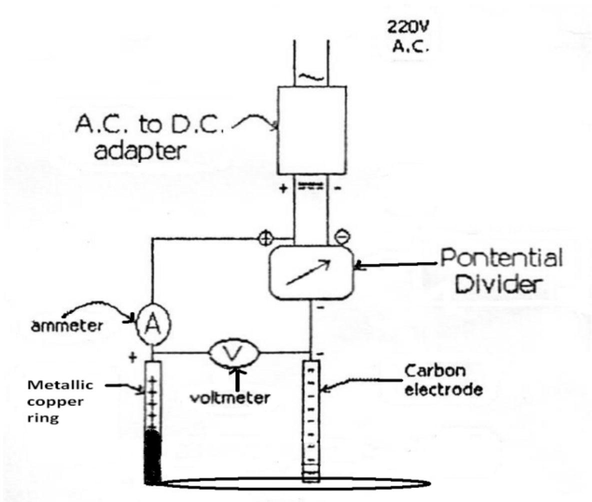


Figure 1. Complete assembly of designed thin layer electrochemical cell

The growing fractal patterns were photographed by using a digital still camera, 14.1 mega pixels, 4 x optical zoom, cyber-shot model no. DSC-W530, SONY. The fractal dimensions of these photographs were measured by using computer software Frac Top v0.3b. SEM images of the copper fractals were also taken by using scanning electron microscopic (SEM) of JEOL from Japan model no. JSM6380A. Samples were coated by quick auto coater model no. JFC-1500 JEOL with gold up to 300 °A.

3. Results and Discussion

The results from experimental observations are discussed both quantitatively and qualitatively in different solvent systems. Copper sulfate of 0.2 mol dm^{-3} was used for the copper fractal formation in aqueous and in aqueous polyvinyl alcohol (0.1 and 1.0 g·dL^{-1}) solvent systems at 10 V potential.

Copper sulfate in aqueous solvent system is dissociated into copper and sulfate ions. Electric field is generated between cathode (carbon rod) and anode (copper wire) when current of particular voltage is applied. Copper ions aggregate around the cathode randomly and deposited as copper metal by gaining two electrons from the electrode.

$$Cu^{2+} + 2e^{-} \rightarrow Cu$$

Growth of copper fractal is an interface controlled crystal growth process. Diffusion limited aggregation (DLA) model provides the basis for the copper fractal formation by electrodeposition. Scanning electron microscopic (SEM) image for surface topography of bounded particles confirmed the presence of fractal structures as shown in Figure 2.

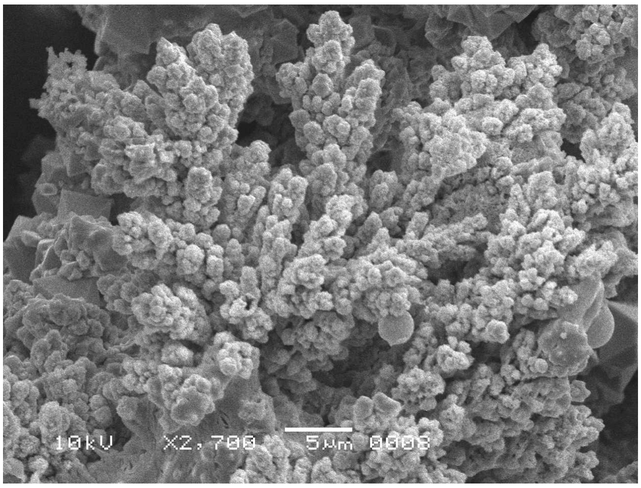


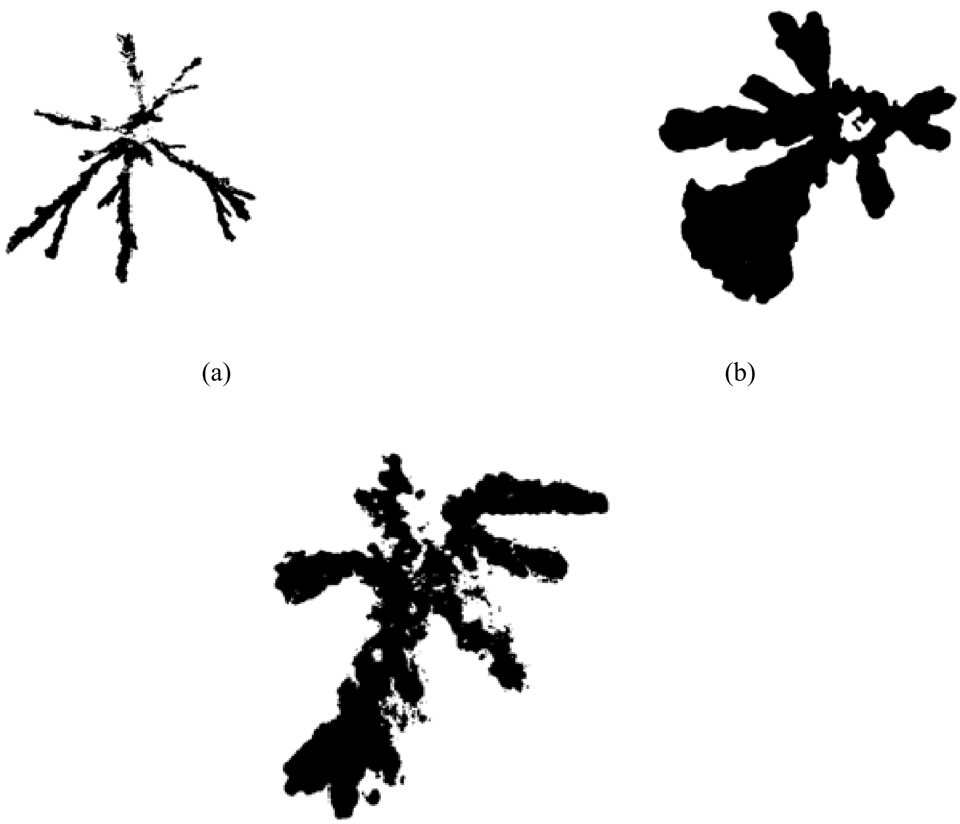
Figure 2. Scanning electron microscopic (SEM) image of copper fractals topography of bounded particles

The change in pattern of copper fractal was observed by varying the composition of PVOH system as shown in Figures 3. It was observed that the growth of fractal in the aqueous system is compact and clear branches were observed while the fractal patterns in 0.5 and 1.0 g·dL^{-1} polyvinyl alcohol systems were diffused. This diffusion in fractal pattern is due to change in diffusion tendency of Cu^{2+} ions in polyvinyl alcohol systems. Copper ions having high charge density orient the surrounding solvent molecules forming a sheath of firmly attached layers. The observed variation in fractal formation with the solution composition explained by the three dimensional structure of the water. It is modified by the addition of PVOH because of its hydrophobic interaction of alkyl chain and hydrogen bonding of hydroxyl group with water molecules (Saeed et al., 2008). From Figure 3, it is also observed that copper fractals possess one nucleation center that propagates in different directions from the nucleation point. They grew irregularly because Cu^{2+} ions walk randomly in solutions obey the Brownian motion mode. As high random motion expected in PVOH solution, may also explain the diffuse structure of fractal at high composition of PVOH.

The fractal dimension is a quantitative parameter which gives information on the mechanistic processes leading to the formation of fractals or the formation of other irregular geometries. Fractal dimension depends on the solvent composition, the processing time and the strength of electric and magnetic fields. The fractal dimension is estimated by using box counting method. The dimension of a fractal measured by a relation:

$$D_f = \log N(l)/\log l \quad (1)$$

where D_f is the fractal dimension, $N(l)$ is the number of boxes with length 'l'. The photographic images were covered by square boxes that vary in size from 2 to 240 pixels. The number of such boxes, 'N' and their size 'l' are used to compute the fractal dimension using the program (Frac Top v0.3b). This program calculates the number of boxes of a particular size needed to fill the space around an image. Each copper fractal image was process with the same procedure. The program then display fractal dimension after plotting a log-log graph between box size versus number of boxes through box counting method. According to Equation (1), the fractal dimension is the slope of the straight line.



(a) (b)

(c)

Figure 3. Photographic images of copper fractals in (a) aqueous solvent system (b) 0.5 g·dL^{-1} aqueous PVOH solvent system (c) 1.0 g·dL^{-1} aqueous PVOH solvent system

Results from the images for the fractal dimension in aqueous and in aqueous polyvinyl alcohol systems are reported in Table 1.

Table 1. Fractal dimension with the solvent composition

Solvent System	Fractal dimension
Aqueous	1.700
0.1 g·dL^{-1} Aqueous PVOH	1.690
0.3 g·dL^{-1} Aqueous PVOH	1.685
0.5 g·dL^{-1} Aqueous PVOH	1.679
0.7 g·dL^{-1} Aqueous PVOH	1.555
1.0 g·dL^{-1} Aqueous PVOH	1.524

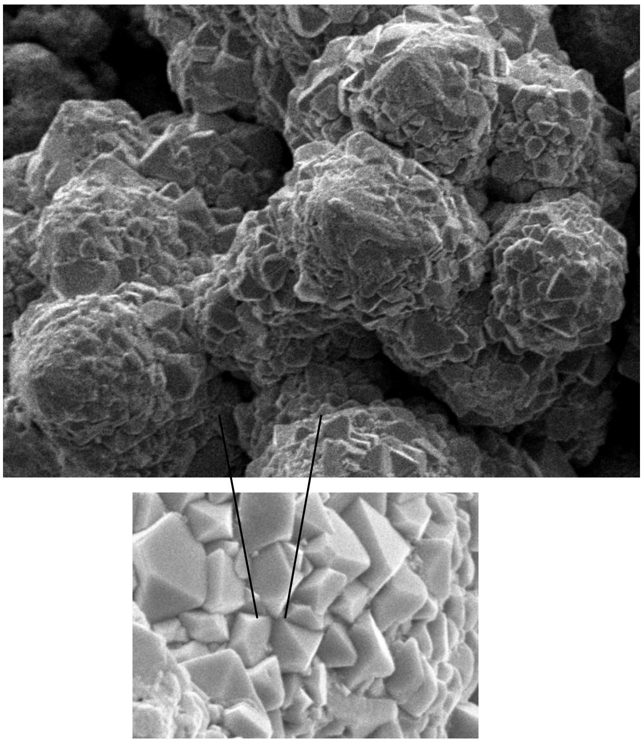


Figure 4. Scanning electron microscopic (SEM) image of copper fractals in aqueous solvent system formed at 10V

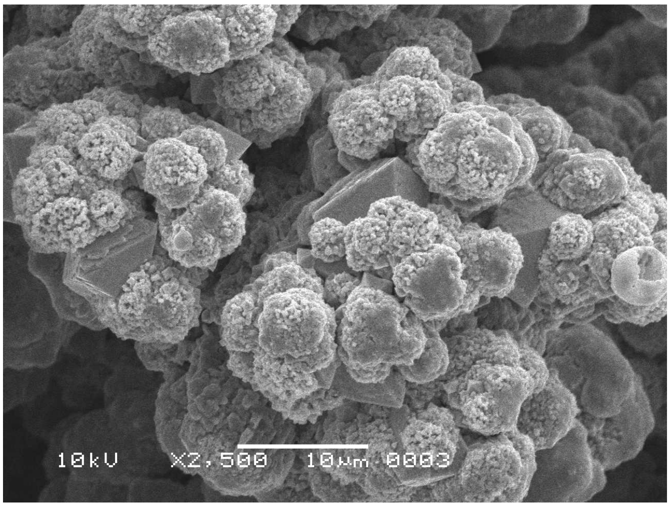
The fractal dimension found to decrease with the increase in polyvinyl alcohol composition. The values of D_f exhibit that the copper fractal dimension in aqueous solvent system is in good agreement with the literature i.e., 1.740.

Copper fractals in aqueous system have a well defined crystalline arrangement of copper particles indicated in Figure 4. In PVOH compositions, instead of crystalline shape, porous flowerlike structures are formed showing randomly distributed spherical clusters arrangement represented in Figure 5. This arrangement of copper fractal in PVOH composition is thin than in aqueous system. This may be attributed due to the decrease in dielectric constant of the medium by the addition of PVOH, while dielectric constant of water favors the dissociation of electrolytes. In aqueous PVOH system, solvent-solvent interactions are higher than the ion-solvent interactions, which causes the decreased dissociation of Cu^{2+} ions. The generated SEM images of Figure 5, also show that fractal aggregation happen in that conditions where high driving forces lead to the generation of the fractals. This driving force is reduced by the introduction of bulky organic molecules which form a viscous medium therefore effect on the fractal dimensions.

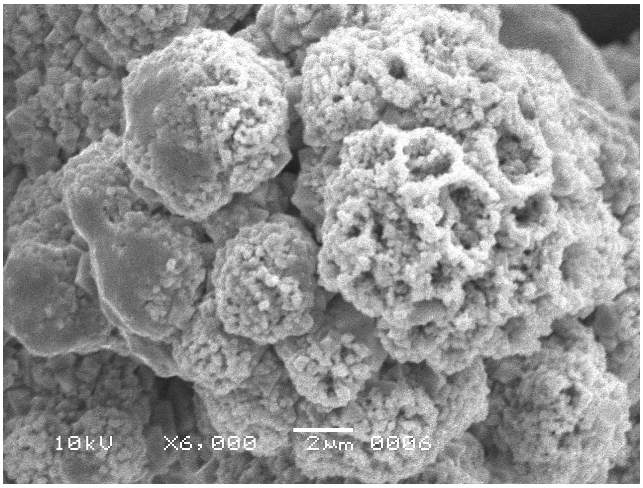
4. Conclusions

Copper fractal growth patterns were studied in aqueous and in aqueous polyvinyl alcohol systems ranging from 0.1 to 1.0 $g{\cdot}dL^{-1}$ at a constant potential of 10 V. These results will be useful for the understanding of solvent effect on the fractal growth pattern. The growth of copper fractal is due to the random ionic motion of copper ions in aqueous and in aqueous solvent system obeying Brownian motion. The decreased in fractal dimension in aqueous polyvinyl alcohol system show that more diffused structure was observed which was also confirmed by the images. The present study will be helpful in the production of a fractal electrode.

(a)



(b)



(c)

Figure 5. Scanning electron microscopic (SEM) image of copper fractals in 1.0 g·dL^{-1} aqueous PVOH system formed at 10 V (a) 10 μm × 2200 (b) at 10 μm × 2500 and (c) at 2 μm × 6000

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References

Ahmad, S., Deepa, M., Sen, V., Kazim, S., & Agarwal, S. K. (2011). Conduction behavior in ionic liquids assisted electrodeposited polypyrrole layers. *Polym. Eng. Sci., 51*, 1513-1518. http://dx.doi.org/10.1002/pen.21946

Akbar, S., Naqvi, I. I., Muhammad, M., & Zahir, E. (2009). Fractal growth of zinc dendrites. *Asian J. Chem., 21*, 4190-4198.

Amir, S., Ali, S. H. A., & Mohamed, N. S. (2011). Ion Conductive polymer electrolyte membranes and simulation of their fractal growth patterns. *Sains Malay., 40*, 75-78.

Andreoli, E., Rooney, D. A., Redington, W., Gunning, R., & Breslin, C. B. (2011). Electrochemical deposition of hierarchical micro/nanostructures of copper hyroxysulfates on polypyrrole-polystyrene sulfonate films. *J. Phys. Chem. C, 115*, 8725-8734. http://dx.doi.org/10.1021/jp200465n

Chen, J. D., & Wilkinson, D. (1985). Pore-scale viscous fingering in porous media. *Phys. Rev. Lett., 55*, 1892-1895. http://dx.doi.org/10.1103/PhysRevLett.55.1892

Cioffi, N., Torsi, L., Losito, I., Di Franco, C., De Bari, I., Chiavarone, L., … Zambonin, P. G. (2001). Electrosynthesis and analytical characterisation of polypyrrole thin filmsmodified with copper nanoparticles, *J. Mater. Chem., 11*, 1434-1440. http://dx.doi.org/10.1039/b009857o

Hatamie, S., Dhole, S. D., Ding, J., & Kale, S. N. (2009). Encapsulation of cobalt nanoparticles in cross-linked-polymer cages. *J. Magn. Magn. Mater., 32*, 2135-2138. http://dx.doi.org/10.1016/j.jmmm.2009.01.014

Ji, Z., Li, H., Liu, Y., Hu, W., & Liu, Y. (2008). The replacement reaction controlling the fractal assembly of copper nanoparticles. *Nanotechnology, 19*, 135602. http://dx.doi.org/10.1088/0957-4484/19/13/135602

Kato, Y., Yokoyama, S., Yabe, T., Ikuta, H., Uchimoto, Y., & Wakihara, M. (2004). Ionic conductivity and transport number of lithium ion in polymer electrolytes containing PEG–borate ester. *Electrochim. Acta, 50*, 281-284. http://dx.doi.org/10.1016/j.electacta.2003.12.066

Murugan, K. D., Amali, J. A., & Natarajan, P. (2012). Formation of fractals by the self-assembly of interpolymer adducts of polymethacrylic acid with complementary polymers in aqueous solution. *J. Chem. Sci., 124*, 375-383. http://dx.doi.org/10.1007/s12039-011-0158-4

Nittmann, J., & Stanley, H. E. (1986). Tip splitting without interfacial tension and dendritic growth patterns arising from molecular anisotropy. *Nature, 321*, 663-668. http://dx.doi.org/10.1038/321663a0

Nittmann, J., & Stanley, H. E. (1987). Non-Deterministic Approach to Anisotropic Growth Patterns with Continuously-Tunable Morphology: The Fractal Properties of Some Real Snowflakes. *J. Phys. A: Math Gen., 20*, 1185-1191. http://dx.doi.org/10.1088/0305-4470/20/17/010

Qi, L., Cölfen, H., Antonietti, M., Li, M., Hopwood, J. D., Ashley, A. J., & Mann, S. (2001). Formation of $BaSO_4$ Fibres with Morphological Complexity in Aqueous Polymer Solutions. *Chem. Eur. J., 7*, 3526-3532. http://dx.doi.org/10.1002/1521-3765(20010817)7:16<3526::AID-CHEM3526>3.0.CO;2-Z

Saeed, R., Masood, S., & Uddin, F. (2008). Ionic interaction of electrolyte with dilute solution of poly (vinyl alcohol) at different temperatures. *Phys. Chem. Liq., 46*, 9-17. http://dx.doi.org/10.1080/00319100601188703

Sakar, D. K., Zhou, X. J., Tannous, A., & Leung, K. T. (2003). Growth mechanisms of copper nanocrystals on thin polypyrrole films by electrochemistry. *J. Phys. Chem. B, 107*, 2879-2881. http://dx.doi.org/10.1021/jp0269524

Teixidor, G. T., Park, B. Y., Mukherjee, P. P., Kang, Q., & Madou, M. J. (2009). Modeling fractal electrodes for Li-ion batteries. *Electrochim. Acta, 54*, 5928-5936. http://dx.doi.org/10.1016/j.electacta.2009.05.060

Zhou, J. G., He, Z., & Guo, J. (1999). Fractal growth modeling of electrochemical deposition in solid freeform fabrication. Proceedings *Tenth Solid Freeform Fabrication Symposium*, Austin, Texas, August.