5.1 INTRODUCTION

Far-from-equilibrium growth phenomena are of much more importance in the development of condensed matter physics and have attracted considerable interest of scientists from various disciplines since the past decade having theoretical and experimental points of view [1-6]. Such experimental and theoretical studies on complex pattern formation include a wide range of problems encompassing life sciences, biology, chemistry, computer sciences, image compression and geology which produce complex geometries of fractal or dendrite character and chaotic patterns.

Aggregation is one of the most familiar phenomena in physical and chemical processes. Continuous efforts have been done to develop the models for fractal growth and aggregation processes. The diffusion limited aggregation model given by Witten and Sander in 1981 [7] has provided a fundamental way to investigate complex pattern formation such as effect of uniform drift and surface diffusion in electro-deposition [8, 9], growth mechanism in thin films [10-12], crystal morphology [13], solidification (snowflakes) [14] and dielectric breakdown (lightning) [15]. Many extensions of DLA model have been developed taking into account the processes involving electrochemical deposition [16], concentration [17], particle drift [18], surface tension [19], sticking probability [20], and heterogeneous surface [21].

Since the last 20 years, fractal growth in polymer electrolyte has attracted much more attention [22-29]. The observation of fractal pattern formation opens new avenues for detailed studies of growth due to a better understanding of the phenomenon without the use of complex theories. Chandra and Chandra [22, 23] were the first to report the technique to grow fractal patterns in polymer electrolyte under bias-free conditions. In our earlier work [28], polymer electrolyte (PEO:NH₄I)
dispersed with Al$_2$O$_3$ as seed particle was used for obtaining the growth under bias free conditions. The growth of fractals was found to be due to the random walk and subsequent aggregation of the mobile species [I$_3^-$ & NH$_4^+$ (via NH$_4^+$I$_3$)]. On approaching the nucleation center, the random walkers stuck and formed an aggregate leading to DLA of different size and varying dimensionality. In another work [29], we reported the effect of electric field on large size fractal growth in polymer electrolyte composites by varying the voltage from 2V – 8V. The application of electric field to the polymer electrolyte composites caused ordered pattern formation in the electric field direction. The growth probability would not be same in all the directions and the above pattern formation was completely governed by convection which was due to the applied voltage. At higher voltages (i.e., at 6V and 8V), there was screening effect on the ions which prohibited the pattern to grow in the electric field direction.

In this chapter, we extended our earlier work reported in chapter 4 by including the influence of low values of electric field on the fractal growth in the polymer electrolyte composites. Subsequently, specified threshold level has been determined below which the growth becomes random and above which the growth is governed by diffusion, convection and migration. The chapter further explores the effect of electric field on the fractal growth by using different kinds of electrode geometry. Different kinds of geometries (parallel, square and circular) have been used to observe the growth under external field. Our results also show the crossover from DBM to chain-like growth to dendritic, i.e., from high field region (A) to constant field region (B) to low field region (C), respectively.

5.2 EXPERIMENTAL

5.2.1 Sample preparation

Samples were prepared by using the solution-cast technique. In this technique, the host polymer (PEO) and salt (NH$_4$I) were weighed in desired weight ratios (i.e., 50:50 wt.%). They were dissolved in distilled methanol thoroughly for ~6-7 hrs. at 40°C. A small amount of activated Al$_2$O$_3$ (neutral, 5 wt.%) was dispersed in the above PEO:NH$_4$I complexed solution. The highly viscous mixture of PEO:NH$_4$I (+Al$_2$O$_3$ (neutral)) obtained after mixing was poured in polypropylene petri-dishes fitted with
different electrode arrangements (viz., parallel, circular and square electrode geometry). For studying the effect of low electric field (i.e., 0–2V) on fractal growth, petri-dishes fitted with parallel electrode geometry were used. The value above threshold was chosen for obtaining the growth in circular and square electrode geometry.

5.3 RESULTS AND DISCUSSION

The physical scenario envisaged is to observe the effect of external field on large size fractal growth in polymer electrolytes as described in our earlier work [29]. The main transport mechanisms involved in growth after application of electric field are diffusion, migration and electro-convective motion. Initially, the polymer electrolyte (PEO:NH₄I) dispersed with Al₂O₃ (neutral) is electrically neutral everywhere with uniform concentration of cations and anions.

(a) Figure 5.1 shows the large size fractal growth after application of 1.5 V between two parallel electrodes which are 30 mm apart. On application of voltage between the electrodes, the cations move towards the cathode where they discharge and collect as H₂. The cations (i.e., protons, as the polymer electrolyte (PEO:NH₄I) is predominantly a proton conductor) which migrate towards the cathode leave behind them a zone of higher pH (i.e., basic front) and near the cathode there is creation of an acidic front. Anions move towards the anode where they pile up since they cannot exit the solution. The whole petri-dish containing the viscous polymer electrolyte composite solution under the influence of electric field is kept in a high humidity environment (R.H. ~ 70% – 80%). High humidity environment gives slow drying rate with enough time for aggregation and the right reducing environment for aggregation to take place. Our earlier work [29] reports that after ~1-2 days, dense branched morphological patterns appear near the anode due to the presence of high concentration of anions near the anode while chain-like growth takes place in the middle part which protrudes in the electric field direction (i.e., towards cathode). Near the cathode, when the growth meets the acidic front, the ordered chain-like growth forms an envelope around the cathode. At the cathode, growth also changes in to dendritic patterns. A well defined angle is then observed between the main branches and the side branches of the dendrites. Nevertheless, the orientation of the branches is only local with no
long range correlation and its distribution in all the directions results in a radial isotropic pattern maintaining an elliptical envelope. The physical model is described by the Nernst-Planck equation for the concentration of cations and anions in the polymer electrolyte subject to diffusion, convection and migration fields. The conventional large size fractal growth in polymer electrolyte composites dispersed with seed particle as nucleation center work doesn’t include electric field as the growth there is completely described by diffusion of ions without any external bias. The growth is a typical laplacian growth as the system is completely under thermal disorder and DLA patterns at different places of different kinds appear. In the current work, it is critical to understand the configuration of the fractal growth having different patterns at different places (i.e., near anode, middle part, near cathode) when an electric field is applied. Here, a qualitative explanation for the phenomenon by using the Nernst Planck equation is being given. Generally, the flux of ions in an electrolyte is completely described by the Nernst Planck equation. The net flux of ions \( j^\pm \) is therefore, the diffusion term \(-D^\pm \nabla c^\pm\), the migration term \( \frac{Z e}{k_B T} D^\pm c^\pm \nabla \Phi\) and the convection term \(c^\pm u\).

\[
    j^\pm = -D^\pm \nabla c^\pm + \frac{Z e}{k_B T} D^\pm c^\pm \nabla \Phi + c^\pm u
\]

where, \(D^\pm\) is the diffusion coefficient of ions, \(c^\pm\), their concentrations, \(\Phi\) electric potential, \(u\) is the fluid velocity and \(\nabla c^\pm\), the concentration gradient.

When the voltage is switched on, a depletion zone of anions occur near the cathode and that of cations near the anode. Meanwhile, an electro-convective motion sets in between the two parallel electrodes. As the speed of an ion in the viscous mixture of the polymer electrolyte composite is simply given by its mobility (\(\mu_c\) for the cation, \(\mu_a\) for anion) times the electric field \(E = \frac{1.5}{3} = 0.5\) V/cm), so, the growth speed of the deposit is equal to the anions mobility times the field. Thus, the migration term and the convection term play key roles in aggregation which is not considered in bias-free aggregation [28]. This is to say, the transport of anions in the aggregation process around the seed particles (Al\(_2\)O\(_3\), neutral) is dominated by diffusion, convection and migration. One should consider the contributions of these
three terms in the aggregation process that lead to different kinds of patterns (i.e., DBM to chain-like growth to dendritic growth) at a fixed distance (i.e., field) from the anode and the cathode.

The forced convection can be neglected due to the absence of any external force. The natural convection arises due to the high humid environment. The local convection arises because of the electro-convective motion that sets in.

Other workers [30] have also demonstrated in electrochemical deposition process that, the migration term \( \frac{z e}{k_B T} D^+ c^+ \nabla \Phi \) could induce DBM, particularly in high field region which is depicted in figure 5.1. In the middle part, the concentration of anions is low as compared to the anode. The contribution of the migration and the convection terms cannot be negligible, hence, in the middle part chain-like growth is observed guided in the direction of electric field due to the electro-convective motion that sets between the two parallel electrodes.

![Figure 5.1: Fractal growth after application of 1.5 V (i.e., E = 0.5 V/cm)](image)
As seen in chapter 4, for higher voltages too, at the cathode, cations form an acidic zone. Chain-like growth which is protruding towards the cathode meets the acidic front which turns the growth into dendritic type of growth. These cations form an envelope around the cathode by making a well defined angle between the main branches and the side branches of the dendrites.

(b) At lower voltages (i.e., at 1 V ($E = \frac{1.0}{3} = 0.333$ V/cm) and at 0.90 V ($E = \frac{0.9}{3} = 0.30$ V/cm)), figure 5.2(a)-(b), the growth looses its directionality in the middle part. This is because the strength of the electric field is not enough to guide the growth.

(c) At further lower voltages (i.e., at 0.85 V ($E = \frac{0.85}{3} = 0.283$ V/cm), at 0.80 V ($E = \frac{0.80}{3} = 0.266$ V/cm) and at 0.50 V ($E = \frac{0.50}{3} = 0.166$ V/cm)), figure 5.2(c)-(e), the growth becomes random. The system behaves like the bias-free aggregation case as reported earlier [28]. The contributions due to migration and electro-convection terms are negligible. The system is completely under thermal disorder and the growth is random. The aggregates are ramified structures with an outer boundary that remains circularly symmetric (especially at low voltages).
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Figure 5.2: Fractal growth in polymer electrolyte: (a) 1V, (b) 0.90 V, (c) 0.85 V, (d) 0.80 V and (e) 0.50 V
After determining the threshold voltage (i.e., 0.90 V) above which effect of electric field on fractal pattern formation (i.e., DBM (near anode), chain-like (middle part), dendritic (near cathode)) takes place in polymer electrolytes, different electrode geometries have been used to simulate the growth. Figure 5.3, figure 5.4 and figure 5.5 shows the growth of polymer electrolyte composites in circular and square electrode geometry.

(a) Circular geometry: After application of electric field between the centre and the circumference of the circle (above threshold, \(E = \frac{3.0}{3} = 1.00\) V/cm), the cations start piling up at the cathode and the anions start piling up at the anode. The ionic transport near the anode could involve a mixture of diffusion, bulk convective motion, and field driven motion which leads to DBM. After that, the growth in the circular electrode geometry is under the influence of two main driving forces namely, the Brownian motion of the ions and the radial ionic motion due to the applied electric field. The growth consists of two components, the random motion and the directional radial movement which leads to chain-like DLA growth with dense branches which protrude in the electric field direction towards the cathode. Thus, the transition occurs from DBM growth to the chain-like growth as the voltage is varied. Growth halts near the cathode due to the presence of the acidic front. There is no transition from the chain-like growth to the dendritic pattern. The experimental observations can be seen in figure 5.3(a)-(e).
Figure 5.3: Fractal growth in circular electrode geometry: (a) without bias, (b) after few hours of applied voltage, (c) after 24 hours of applied voltage, (d) after 2-3 days & (e) after complete growth
In case of reverse polarity, there is no formation of DBM patterns since there is no accumulation of anions near the anode. After application of the electric field, anions uniformly distribute around the circumference of the circle and the cations towards the cathode. So, an acidic zone is created near the center. Only chain-like growth pointing towards in the electric field direction is observed as shown in figure 5.4(a)-(c).
Square geometry: After application of electric field (above threshold, \( E = \frac{2.0}{3} = 0.666 \) V/cm), there is separation of ions and the anions pile up at the anodes. Cations pile up at the cathodes which lead to \( \text{H}_2 \) bubbles as shown in figure 5.5(b). The experimental observation for growth under square geometry can be seen in figure 5.5(a)-(f). Figure 5.5(c) depicts the aggregation of anions near the anode as a consequence of which the shape of the electrode changes effectively from planar to irregular. Thus, after a few days of applied bias, the DBM patterns near the high concentration of anions (i.e., region A, figure 5.5(e)) and the chain-like growth start protruding towards the electric field direction within the square region (i.e., region ‘B’). The growth of dendritic patterns appears at low concentration of anions (i.e., near the cathode (region ‘C’)).
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(c)

(d)
Figure 5.5: Fractal growth using square electrode geometry: (a) without bias, (b) after 2 minutes of applied voltage, (c) after 24 hours, (d) after 3 days, (e) after 4-5 days and (f) after complete growth.
5.4 CONCLUSIONS

It has been seen that the fractal growth between two electrodes depends only on the distance separating the two electrodes, i.e., the electric field per unit length. The threshold field has been found to be 0.30V/cm. Below the specified threshold, the growth is random (i.e., bias-free aggregation). Above the specified threshold, fractal growth kinetics is a combined effect of many competing processes, viz., Brownian motion due to thermal agitation (high humid environment), electro-convective motion, and very high local electric field near the tips of the aggregate. Thus, the combined effect of diffusion, electro-convection and migration, leads to the aggregates to undergo morphological transitions from DBM to chain-like growth to dendritic pattern. The ion diffusion phenomenon that leads to large size fractal growth after the application of electric field has been analyzed on the basis of the mass transfer equation. Voltages greater than the threshold value have been chosen to obtain the growth using parallel, square and circular electrode geometry. To the best of our knowledge, this phenomenon has not been reported earlier. This will help in a better understanding of morphogenesis of fractal growth kinetics in ion conducting polymer electrolyte without the use of complicated equations and theories.
5.5 REFERENCES


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