Electric field driven fractal growth dynamics in polymeric medium

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A B S T R A C T

This paper reports the extension of earlier work (Dawar and Chandra, 2012) [27] by including the influence of low values of electric field on diffusion limited aggregation (DLA) patterns in polymer electrolyte composites. Subsequently, specified cut-off value of voltage has been determined. Below the cut-off voltage, the growth becomes direction independent (i.e., random) and gives rise to ramified DLA patterns while above the cut-off, growth is governed by diffusion, convection and migration. These three terms (i.e., diffusion, convection and migration) lead to structural transition that varies from dense branched morphology (DBM) to chain-like growth to dendritic growth, i.e., from high field region (A) to constant field region (B) to low field region (C), respectively. The paper further explores the growth under different kinds of electrode geometries (circular and square electrode geometry). A qualitative explanation for fractal growth phenomena at applied voltage based on Nernst–Planck equation has been proposed.

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1. Introduction

Pattern formation, i.e., the non-equilibrium growth phenomenon, has attracted considerable interest of scientists from various disciplines in the past decade. Such far from equilibrium growth studies include a wide range of problems encompassing life sciences, physics, biology, chemistry, computer science, image compression and geology which produce complex geometries of fractal or dendrite character and chaotic patterns [1–4].

Aggregation is one of the most familiar phenomena in physical and chemical processes. Many efforts have been made to develop models for fractal growth and aggregation processes [2]. Among these models, the most well known one is diffusion limited aggregation (DLA). The DLA model was proposed in 1981 by Witten and Sander as a computer algorithm [5]. In this model, aggregation process begins with fixing one particle at the center of coordinates in 2 dimensions and follows the formation of cluster by releasing particles from infinity. The particles undergo random walk due to Brownian motion until they hit any particle belonging to the growing cluster and stick to it. The DLA model has since attained a paradigmatic status due to its simplicity and presents the fundamental way for many diffusive systems such as effect of uniform drift and surface diffusion in electrodeposition [6,7], dielectric breakdown (lightening) [8], viscous fingering [9,10], growth mechanism in thin film [11], crystal morphology [12] and solidification (snowflakes) [13]. Many extensions of DLA model have

been developed taking into account the processes involving concentration [14], particle drift [15], surface tension [16], sticking probability [17], and heterogeneous surface [18].

In polymer science, polymer growth is a fractal process [19]. Since the last 20 years, fractal growth in polymer electrolyte has attracted much more attention [20–27]. The observation of fractal pattern formation opens new avenues for detailed studies of growth due to the better understanding of the phenomenon without the use of complex theories. Chandra and Chandra [20,21] were first to report the technique to grow fractal patterns in polymer electrolyte under bias-free conditions. They reported the fractal growth in ion conducting polymer due to random walk of ions and their subsequent aggregation around nucleation centers. Recently, another group of researchers [22–25] also cultured fractals in various ion conducting polymer electrolyte membranes experimentally. They also did theoretical modeling of the experimentally cultured fractals. In our earlier work [26], polymer electrolyte (PEO:NH$_4$I) dispersed with Al$_2$O$_3$ as a 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$_3^-$ and 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 sizes and varying dimensionality. In another work [27], we reported the effect of electric field on large size fractal growth in polymer electrolyte composites by varying the voltage from 2 V to 8 V. 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 the same in all the directions

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and the pattern formation was completely governed by convection which was due to the applied voltage. At higher voltages (i.e., at 6 V and 8 V), there was screening effect on the ions which prohibited the pattern to grow in the electric field direction.

In the present work, electric field induced aggregation in polymer electrolyte composites has been studied under the influence of low values of electric field and extends the earlier reported work [27]. Specified threshold level has been determined. Below the threshold, the growth becomes random and above the threshold, the growth is governed by diffusion, convection and migration. Different kinds of electrode geometries have been used to simulate the growth under external field.

2. Experimental setup

2.1. Sample preparation

Samples were prepared by using the solution-cast technique. In this technique, the host polymer (Poly (ethylene oxide) (PEO), Sigma-Aldrich, Mol. Wt. $\sim 6 \times 10^5$) and salt (NH_4I (Sigma Aldrich, 99.999% trace metals basis)) were weighed in desired weight ratio (i.e., 50:50 wt.%). They were dissolved in distilled methanol thoroughly for $\sim$6–7 hr at 40 °C. A small amount of activated Al_2O_3 (neutral, 5 wt.% (Sigma-Aldrich, pH = 7.0 ± 0.5 (in H_2O))) was dispersed in the above PEO:NH_4I complexed solution. The highly viscous mixture of PEO:NH_4I (+Al_2O_3 (neutral)) obtained after mixing was poured in polypropylene Petri-dishes (diameter = 7.5 cm) fitted with different electrode arrangements (viz. parallel, square and circular electrode geometry). The applied potential difference V across the electrode was varied from 0 to 2 V. The parallel electrodes were separated by a distance of 30 mm.

3. Results and discussion

The physical scenario envisaged is the effect of external field on large size fractal growth in polymer electrolyte. The main transport mechanisms involved in the growth after application of electric field are diffusion, migration and electro-convective motion. Initially, the polymer electrolyte (PEO:NH_4I) dispersed with Al_2O_3 (neutral) is electrically neutral everywhere with uniform concentration of cations and anions.

(a) Fig. 1 shows the large size fractal growth after application of 1.5 V between two parallel electrodes. On application of voltage between the electrodes, the cations move towards the cathode where they discharge and act as a collection center for H_2. The cations (i.e., protons, as the polymer electrolyte (PEO:NH_4I) 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, provides enough time for aggregation and the right reducing environment for aggregation to take place. Earlier work [27] has reported 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 patterns meet the acidic front, the ordered chain-like growth forms an envelope around the cathode. At the cathode, growth also changes to dendritic patterns. A well defined angle is then observed between the main branches and the side branches of the dendrites. However, the orientation of the branches is only local with no long range correlation and their distribution
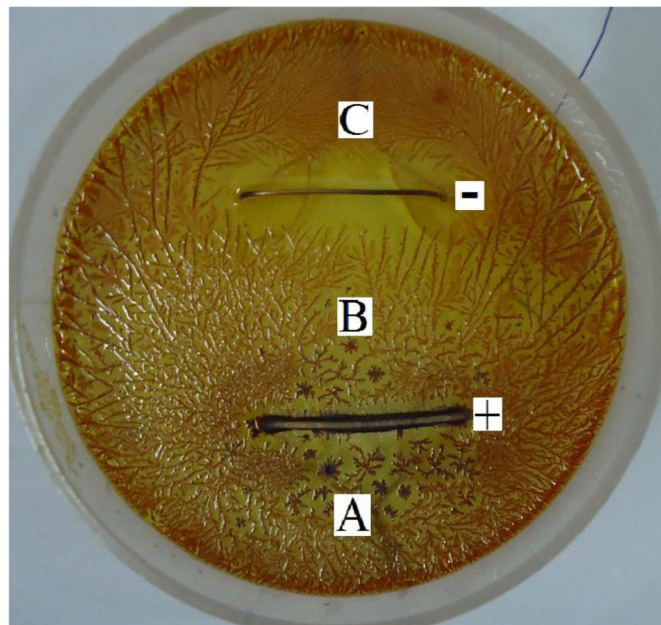

Fig. 1. Fractal growth after application of 1.5 V (i.e., $E = 0.5$ V/cm).

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 composite dispersed with seed particle does not include electric field since the growth there is completely governed by diffusion of ions in the polymer electrolyte without any external bias [26]. 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, in the 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 ($\frac{ze}{K_B T}D^{\pm}c^{\pm}\nabla\Phi$) and the convection term ($c^{\pm}u$) [28].

$$j^{\pm} = -D^{\pm}\nabla c^{\pm} + \frac{ze}{K_B T}D^{\pm}c^{\pm}\nabla\Phi + c^{\pm}u \qquad (1)$$

where $D^{\pm}$ is the diffusion coefficient of ions, $c^{\pm}$ their concentrations, Φ electric potential, u is the fluid velocity and $\nabla c^{\pm}$ the concentration gradient.

Consider the Petri-dish containing two parallel electrodes and assume that the aggregation is proceeding slowly in quasi stationary state governed by diffusion, convection and migration in an electric field. The component of electric field parallel to the electrodes will be zero (i.e., the electric field in the x-direction, $E_x = 0$). Thus, the second term denotes only migration in the electric field in the y-direction. When the voltage is switched on, a depletion zone of anions occurs near the cathode and that of cations near the anode. Meanwhile, an electro-convective motion sets in between the two parallel electrodes. The speed of an ion in the viscous mixture of polymer electrolyte composite is given by its mobility (μ_c for the cation, μ_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 anion's mobility times the field. Thus, the migration term and the convection term play key roles in aggregation which is not