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Ion Conductive Polymer Electrolyte Membranes and Simulation of Their Fractal Growth Patterns

(Membran Polimer Elektrolit Konduksian Ion dan Simulasi Pola-pola Pertumbuhan Fraktal)

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ABSTRACT

Due to their high ionic conductivity, solid polymer electrolyte (SPE) systems have attracted wide spread attention as the most appropriate choice to fabricate all-solid-state electrochemical devices, namely batteries, sensors and fuel cells. In this work, ion conductive polymer electrolyte membranes have been prepared for battery fabrication. However, fractals were found to grow in these polymer electrolyte membranes weeks after they were prepared. It was believed that the formation of fractal aggregates in these membranes were due to ionic movement. The discovery of fractal growth pattern can be used to understand the effects of such phenomenon in the polymer electrolyte membranes. Digital images of the fractal growth patterns were taken and a simulation model was developed based on the Brownian motion theory and a fractal dialect known as L-system. A computer coding has been designed to simulate and visualize the fractal growth.

Keywords: Fractal; polymer electrolytes; simulation

ABSTRAK

Disebabkan kekonduksian ionik yang tinggi, sistem polimer elektrolit pepejal (SPE) telah menarik perhatian meluas sebagai pilihan paling sesuai untuk memfabrikasi alat elektrokimia keadaan pepejal sepenuhnya, iaitu bateri, pengesan dan sel bahan bakar. Dalam kerja penyelidikan ini, membran polimer elektrolit konduksian ion telah disediakan untuk penyediaan bateri. Bagaimanapun, fraktal telah didapati tumbuh dalam membran polimer elektrolit ini beberapa minggu selepas disediakan. Adalah dipercayai pembentukan agregat fraktal dalam membran ini ialah disebabkan oleh pergerakan ion. Penemuan corak pertumbuhan fraktal boleh digunakan bagi memahami kesan fenomena pergerakan ion dalam membran polimer elektrolit. Imej-imej digital pola-pola pertumbuhan fraktal telah diambil dan satu model simulasi dibangunkan berasaskan teori pergerakan Brown dan dialek fractal dikenali sebagai L-sistem. Pengekodan komputer telah direkabentuk bagi mensimulasi dan menggambarkan pertumbuhan fraktal.

Kata kunci: Elektrolit polimer; fraktal; simulasi

INTRODUCTION

By definition, an ion-conducting polymer is a polymeric material that exhibits high ionic conductivity but low electronic conductivity (Horie et al. 2004). Potential applications for conducting polymers are numerous in devices such as fuel cells, supercapacitors, sensors, electrochromic displays and solar cells (Stephan 2006). Since metals are toxic and can damage the environment (Harun et al. 2007), conducting polymers are the better alternatives.

Hence, many researchers have been putting their time and effort to produce improved polymer electrolyte materials especially in the development of batteries. However, for quite some time, polymer electrolytes have also been found to be sort of media for fractal growth (Amir et al. 2008; Chandra 1996; Chandra & Chandra 1994).

Electrochemical electrodeposition (Barkey 1991), electrochemical polymerization (Chandra 1996) and diffusion limited aggregation growth structures of many metal aggregates in the presence of a magnetic field as external stimuli (Kaufmann et al. 1987) have been well suited with many fractal growth models. Thereof, a few group of researchers (Amir et al. 2007; Amir 2008; Amir et al. 2010; Mohamed & Arof 2001; Okubo et al. 1993) have also reported the formation of fractals without using any external stimuli. In this work, fractals were observed in two polymer electrolyte systems, Poly(vinylidenefluoride-co-hexafluoropropylene)/Poly(ethylmethacrylate)-ammonium trifluoro- methane sulfonate (PVDF-HFP/PEMA-$NH_4CF_3SO_3$) dispersed with Cr_2O_3 and *polyethylene oxide-ammonium iodide* (PEO-NH_4I). It was indicated that the growth of these fractals is due to the diffusion of ions in the host polymer matrices. The objectives of this work are to study the fractal growth in ion conductive polymer electrolyte membranes and to simulate the fractal observed using suitable techniques. For that purpose, a computerize based model has been created to simulate and visualize the growth of these fractal patterns.

Materials and Methods

Preparation of Materials

The polymer electrolyte membranes used as media to culture fractals were prepared separately by using the solution casting method. In this preparation, PEO (M_w = ~6×10^5) and NH_4I were weighed according to the desired PEO:NH_4I weight ratios and dissolved in 100 mL methanol while PVDF-HFP, PEMA and NH_4CF_4 of fixed w% ratio were dissolved in N-N dimethyl formamide (DMF) using digital magnetic stirrers. Appropriate weight percentage of Cr_2O_3 in nanosize was added specifically to the PVDF-HFP, PEMA and NH_4CF_4 solutions. In each preparation, the solution was stirred for a few hours until homogeneous solutions were obtained. The solution that had completely dissolved was then cast into petri dishes and left to dry slowly at room temperature in a dark and dry place for several weeks. After drying, fractal patterns were observed and their digital images were taken.

Simulation Methods

A fractal dialect called L-systems (Prusinkiewicz & Lindenmayer 2004) was implemented into the simulation applying the 'Brownian motion' theory. L-Systems rules' recursive nature leads to self-similarity and its simple string-based commands allow easy description of such complex geometric patterns particularly fractal growth patterns. By increasing the recursion level, a form slowly, grows' and becomes more complex, as can be seen in diffusion-limited aggregation (DLA) models (Witten & Sander 1981) and natural-looking organic forms. The rules of the L-system grammar are applied iteratively starting from the initial state which is called the axiom and a set of production rules.

To compare the simulation with the real patterns obtained, one vital aspect would be the calculation of their fractal dimension values. The box-count method was used to calculate the fractal dimension of the DLA structure identified in this research as a clear representation of a random fractal that generates a stochastic fractal growth pattern (Kleinert 2004).

Discussion

The fractal patterns in PVDF-HFP/PEMA-$NH_4CF_3SO_3$-Cr_2O_3 and PEO-NH_4I polymer electrolyte membranes are shown in Figure 1. Their digital photos were taken, pre-processed via an image processing software and uploaded to the fractal dimension determination computer software tool (Suki et al. 2007). From Figure 1, it is observed that fractals are formed at different nucleation centers and then grew in certain directions away from the nucleation sites. They grew irregularly and in an unpredictable motion which can be attributed to the Brownian motion of aggregating species.

For simulation purposes, six fractal aggregates each from PVDF-HFP/PEMA-$NH_4CF_3SO_3$-Cr_2O_3 and PEO-NH_4I polymer electrolyte membranes were selected. Their respective simulated patterns are shown in Figure 2.

The fractal dimensions for all of the experimentally cultured and simulated fractals are listed in Tables 1 and 2. The tables show that the fractal dimension values of the experimentally cultured fractals are in good agreement with the fractal dimension values obtained from their respective simulated ones.

Conclusion

Other than being potential materials for applications in various electrochemical devices, ion conductive polymer electrolyte membranes are also suitable for the study of fractals. The growth of fractals observed in this study is due to the random motion of aggregating species. Evidently, the simulation model which is based on the Brownian motion theory and a fractal dialect known as L-system is congruent to fractals cultured in the ion conductive polymer membranes. Further research is to be carried out

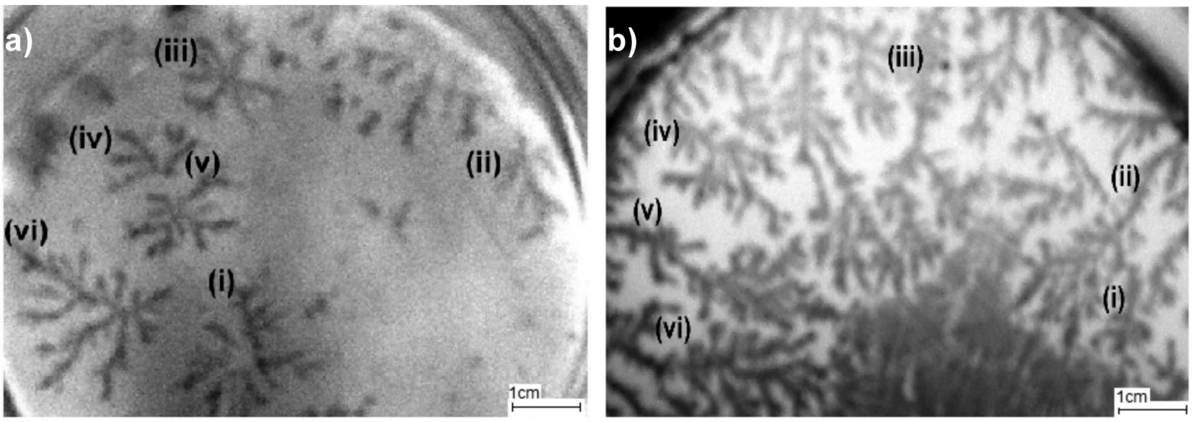

FIGURE 1. Digital images of the fractal patterns observed in (a) PVDF-HFP/PEMA-$NH_4CF_3SO_3$-Cr_2O_3 and (b) PEO-NH_4I membranes

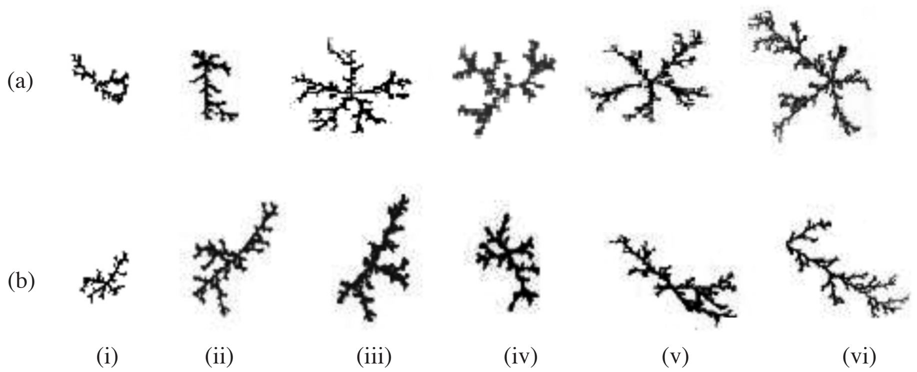

FIGURE 2. The simulated fractal patterns

TABLE 1. Fractal dimension values of the experimentally cultured fractal patterns as shown in Figure 1(a) and their respective simulated fractal patterns, Figure 2(a)

Cultured Fractals	Fractal Dimension	Simulated Fractals	Fractal Dimension
Fig. 1(a)(i)	1.718 ± 0.045	Fig. 2(a)(i)	1.720 ± 0.043
Fig. 1(a)(ii)	1.731 ± 0.042	Fig. 2(a)(ii)	1.735 ± 0.046
Fig. 1(a)(iii)	1.749 ± 0.043	Fig. 2(a)(iii)	1.753 ± 0.042
Fig. 1(a)(iv)	1.743 ± 0.049	Fig. 2(a)(iv)	1.748 ± 0.047
Fig. 1(a)(v)	1.757 ± 0.041	Fig. 2(a)(v)	1.753 ± 0.045
Fig. 1(a)(vi)	1.786 ± 0.046	Fig. 2(a)(vi)	1.771 ± 0.041

TABLE 2. Fractal dimension values of the experimentally cultured fractal patterns as shown in Figure 1(b) and their respective simulated fractal patterns, Figure 2(b)

Cultured Fractals	Fractal Dimension	Simulated Fractals	Fractal Dimension
Fig. 1(b)(i)	1.714 ± 0.051	Fig. 2(b)(i)	1.723 ± 0.045
Fig. 1(b)(ii)	1.753 ± 0.042	Fig. 2(b)(ii)	1.755 ± 0.042
Fig. 1(b)(iii)	1.741 ± 0.035	Fig. 2(b)(iii)	1.746 ± 0.043
Fig. 1(b)(iv)	1.748 ± 0.045	Fig. 2(b)(iv)	1.745 ± 0.041
Fig. 1(b)(v)	1.759 ± 0.052	Fig. 2(b)(v)	1.757 ± 0.044
Fig. 1(b)(vi)	1.778 ± 0.054	Fig. 2(b)(vi)	1.769 ± 0.048

to improve the computer algorithm used in the simulation model in order to get better results.

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