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LETTER TO THE EDITOR

The growth of dendrites of fractal pattern on a conducting polymer

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Abstract. Dendrite, of fractal pattern, has been observed on the surface of the conducting polymer polypyrrole, after an 'undoping' process. Metal ions have been deposited on the surface of the conducting polymer by applying a voltage for undoping. The fractal dimension has been calculated from the self-correlation function. The growth mechanism of the dendrite has been explained on the basis of the DLA model and the undoping process.

Conducting polymers with a molecular structure composed of a highly extended conjugated π-electron system have attracted much attention as regards both scientific interest and technical applications, since physical properties such as conductivity, magnetic susceptibility and optical absorption are changed drastically by the 'dope–undope' process [1, 2]. Various types of application of the conducting polymer have also been proposed: as a secondary battery [3, 4], as an optical switching element [5, 6], as a memory device [7, 8], as a sensor [9, 10] etc.

The electrochemical polymerization method is one of the simplest and most convenient methods of preparation of thin films. The thickness and the area of the film are easily controlled by this method. Furthermore, conducting polymers are easily doped and 'undoped' by an electrochemical method, by controlling the polarity and current.

The dope–undope process is important for applications of conducting polymers. The formation of the dendrite strongly affects the lifetime of the secondary battery, the optical switching element etc. In general, the dendrite grows from the surface of the conducting polymer to the counter-electrode in the solvent, and bridges both electrodes, resulting in the failure of the operation.

When the change of the surface morphology was investigated under the dope–undope process, another type of dendrite was observed. A number of the dendrites spread on the surface of the conducting polymer. These patterns looked like the pattern of a diffusion-limited aggregation (DLA) obtained by computer simulation [11]. A similar phenomenon was observed in sputter-deposited $NbGe_2$ films [12].

In this letter, the dendrite pattern on the conducting polymer is reported, and the growth mechanism of the dendrite is discussed. In addition, the fractal dimension was also evaluated.

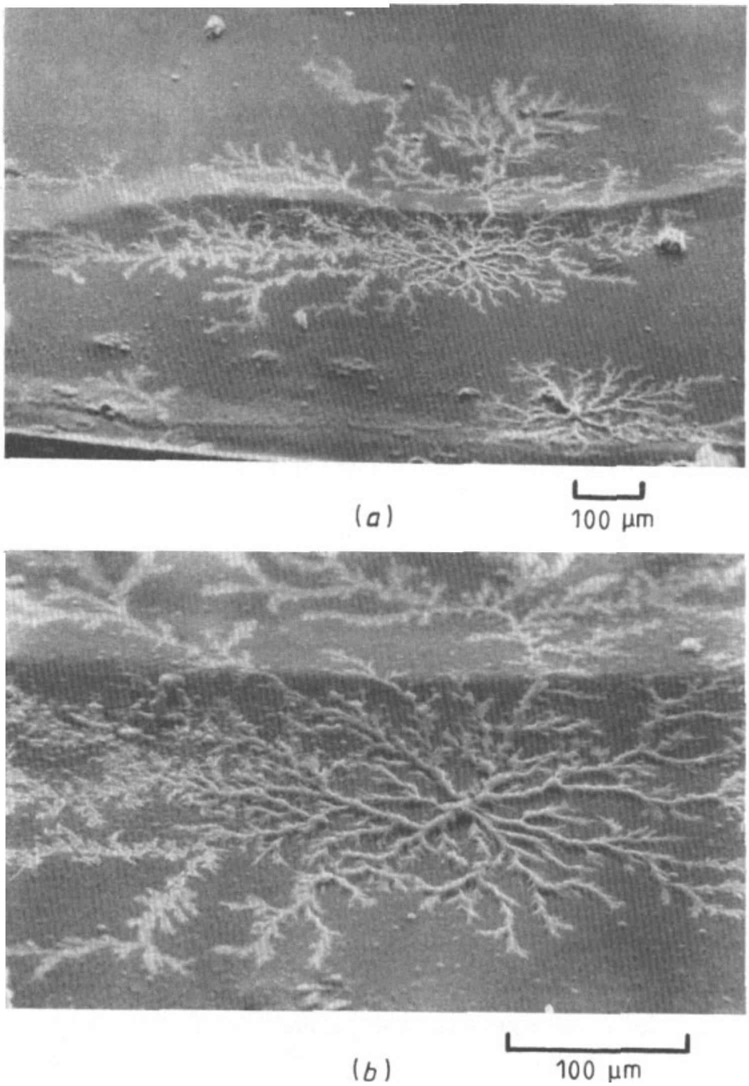

Figure 1. SEM photographs of the surface on the conducting polymer: (*a*) a few dendrite growths; and (*b*) the centre part of the dendrite growth.

The experimental method was as follows. A polypyrrole film ($\approx 1 \times 2\ cm^2$) was prepared electrochemically on an In–Sn oxide (ITO) conducting glass substrate in an electrolyte solution (0.5 mM *p*-toluenesulphonate in 0.5 mM acetonitrile + 1% H_2O with 0.1 M monomer, pyrrole). A nickel plate the same size as the ITO glass electrode was used as a counter-electrode. At first, a voltage of 3 V was applied between the two electrodes for three hours. Half of the electrolyte solution was poured out from the cell and the bottom part of the polypyrrole was made to become undoped for 1.5 h at the reversed applied voltage of 3 V. The undoped surface was observed with a scanning electron microscope (Akasi ALPHA-10).

The fractal dimension was evaluated as follows [13, 14]. The pattern obtained was transferred onto a microcomputer (EPSON PC-286VF) with an image scanner. The self-correlation function, $C(r)$, of the pattern was calculated using a fast-Fourier-transform

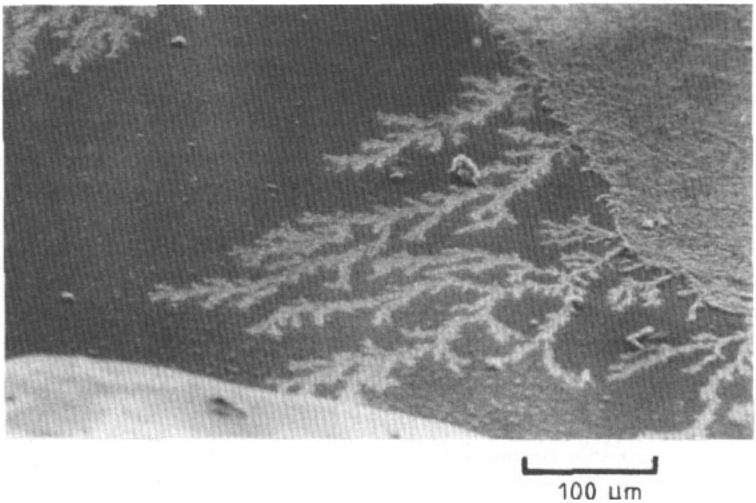

Figure 2. An SEM photograph of the surface on the conducting polymer. The branches grown from the pond-like dendrite (upper right).

technique, where r is the distance measured in pixel units. If the pattern has a fractal structure, then its correlation function is represented by $C(r) \sim r^{-A}$. Thus its fractal dimension, $D = 2 - A$, is obtained.

The results are now described. Figure 1 shows the SEM photographs of the surface of the undoped conducting polymer. A few dendrite growths spread on the surface are shown in figure 1(a). Each pattern looks like the DLA pattern obtained by computer simulation. Figure 1(b) shows the centre part of the dendrite growth. The branches near the centre are rod-like although the branches near the top of the growth are flat. The branches grown from the pond-like deposit were also observed as shown in figure 2. These dendrite growths do not protrude into the solution, although the dendrite growth that has been generally observed in the secondary battery protrudes.

Since the pattern seemed to be a fractal, the self-correlation function was calculated. Figure 3 shows the self-correlation function of the dendrite growth that is at the centre position in figure 1(a). The linearity appears within the range indicated by two arrows, which indicates the fractal region, but the pattern is not fractal as a whole. In this case, the pattern is statistically self-similar in the small region and its fractal dimension is 1.69.

Nickel could be the deposited product at the surface of the conducting polymer, although a detailed elemental analysis has not been completed. In the electrodeposition experiment, the same pattern of nickel dendrite is also reported [15].

The growth mechanism of the dendrite on the surface of the conducting polymer is considered as follows by taking the undoping process into account. Figure 4 shows the model of the dendrite growth near the surface of the conducting polymer. When the reverse voltage is applied between the nickel and the conducting polymer electrode, nickel ions are attracted to the surface of the conducting polymer. Here the reverse voltage refers to the polarity of the applied voltage, so the conducting polymer is undoped. That is, the conducting polymer and the nickel plate are of negative and positive polarity, respectively. The ions, which are indicated as particles B in figure 4, move around the surface since they have thermal energy. The conducting polymer is

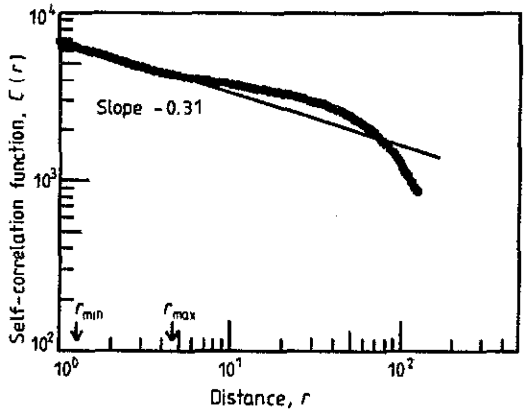

Figure 3. The self-correlation function of the dendrite growth that is at the centre position in figure 1(*a*). *r* is measured in pixel units, 2.6 μm/pixel. Two arrows indicate the region of linear slope of *C*(*r*) where the self-similarity is established.

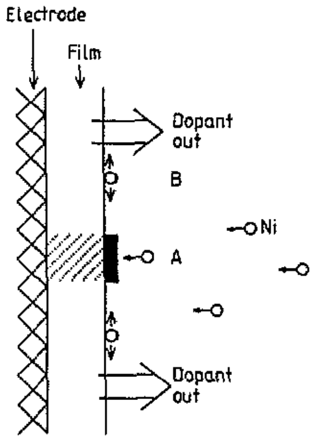

Figure 4. The model of the growth mechanism of the dendrite; schematic side view near the surface of the polymer. The nickel ion deposits on part A of the conducting polymer where the conductivity is kept high. The nickel ions, B, walk randomly on the surface, with thermal energy.

undoped and its conductivity decreases. However, the conductivity in some regions is kept high since the conducting polymer film is not uniformly undoped with time. The nickel ion, therefore, deposits on part A of the surface with higher conductivity, as shown in figure 4. The deposits become the seeds. In the next step, when the nickel ion, which walks randomly on the surface of the polymer, encounters the seed, it is deposited, and thus the dendrite grows. The same process is repeated at the same time, and thus other dendrites also grow, starting from other points. If the area of the part with high conductivity is large, the seed becomes pond-like.

It should be noted that the dendrites grown not only in the electrolyte solution but also on the surface must be considered when the dope–undope process is repeated.

In conclusion, dendrite with a fractal pattern was observed on the surface of the conducting polymer polypyrrole, during the electrochemical undoping process. It was deposited on the surface of the conducting polymer by using a reverse-applied voltage of 3 V. That is, polypyrrole is negative. Two types of dendrite were observed: (i) the DLA-like dendrite; and (ii) the dendrite composed of branches and a pond-like deposit. The fractal dimension has been calculated using the self-correlation function. A growth mechanism for the dendrite on the surface was proposed.

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