

Control of Crystallinity and Morphology of Polyaniline by Electrochemically Synthetic Condition

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We researched how to control the aggregation of polyaniline, one of conductive polymers that can be synthesized electrochemically. The crystallinity of polyaniline synthesized electrochemically at various distance between the electrodes was estimated by X-ray method. Commercial conductive papers were used for the simulation of the electric field in the actual electrolytic cell. It was found that the strong and vertical electric field around the working electrode exerted the effect on the control of high crystallinity of polyaniline.

key words: polyaniline, crystallinity, electrochemical synthesis

1. INTRODUCTION

Polyaniline (PAn) is one of conductive polymers and has been employed practically as materials for electrodes of secondary batteries and so on. In general, electronic properties of materials depend on their states of aggregation, such as crystallinity. We reported previously that PAns in orderly form (observed with SEM) had lower λ_{\max} of UV absorption spectra than those in disorderly form¹⁾. However, it is not very easy to control the aggregation of polymers. It also means to be difficult to control the electronic properties of such polymers. Some researchers have been making efforts for the control of aggregation of PAn and other conductive polymers in various ways^{2),7),8),9),10)}. Recently, Ito et al have developed the approach to grow the single crystals of PAn from solution²⁾. There are few papers to control the crystallinity of PAn at synthetic stages. In our previous paper¹⁾, we reported that the configuration of the electrolytic cell influenced the morphology of PAn synthesized electrochemically. It showed the possibility to control the aggregation of PAn synthesized electrochemically by controlling the electric field. It has been known that the electric field around the working electrode influence

the metal deposition types during electroplating¹¹⁾.

In the present work, we estimated the crystallinity of PAn, as a factor of the aggregation, deposited at various positions on the electrode for various distances between the electrodes. On the other hand, the actual electric field in the electrolytic cell was simulated, using commercial conductive papers. Our objective was to determine whether the electric field effected on increasing of the crystallinity of PAn synthesized electrochemically, as well as the metal deposition during electroplating.

2. EXPERIMENTAL

All the chemicals used in this study were of reagent grade. The aqueous solution containing 1.0mol/dm³ aniline and 2.0 mol/dm³ hydrochloric acid was degassed with nitrogen gas and used as electrolyte to synthesize PAn as described in the previous paper. Pt plates (20x30mm in size) were used as the working and counter electrodes. These electrodes were arranged to face each other in parallel, varyng the distance between them, d, from 10 to 40mm in order to change the electric field around the working electrode.

PAn was synthesized under the potentiostatic

condition up to reaching a given amount of electricity, 100 Coulomb. The constant potential +0.80V vs. Ag/AgCl saturated KCl reference electrode was employed as described in the previous papers^{1),3),4),5)}. The position of usual salt bridge joining the reference electrode to the working electrode was fixed even at various d .

The crystallinity of PAN deposited at every position on the electrode was evaluated by X-ray method after collecting and drying. The morphology of PAN were observed with SEM.

The simulation of the electric field was carried out by the classical method using commercial conductive papers⁶⁾. That is, the equipotential lines were made by measuring the potentials at various positions on the conductive paper model of the cell. The conductive papers were provided by Uchida Techno Service Co.,(No. 193-1212).

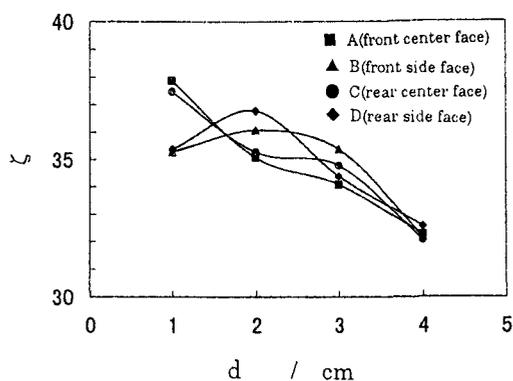


Fig.1 The plots of crystallinity ζ of PAN against electrodes distance d . A (front center face) is for PAN grew at center of the working electrode surface to face the counter electrode, B (front side face) for in side of the same surface to face to the counter one. In the same manner, C (rear center face) and D(rear side face) represent the center and side position, respectively, of the another surface of the working electrode.

3. RESULTS AND DISCUSSION

All the X-ray patterns of PANs obtained in this study showed the characteristic 5 peaks of the emeraldine salt doped with HCl: (001), (010), (100), $\{(110)\}$ and $\{(111)\}$ ¹²⁾. Figure 1 shows the

plots of the crystallinity ζ against d . The ζ in this figure are the values which were estimated relatively from X-ray peak area, using the 5 peaks described above. Since neither completely crystalline nor completely amorphous PAN was not obtained, by treating the PAN's X-ray data with smallest peaks among our data as 'amorphous' PAN's data, ζ values were estimated. The 'amorphous' PAN was synthesized at large d and for much quantity of electricity ($d=40\text{mm}$, 400Coulomb), not to grow crystals. Then the absolute crystallinity values used in the figure should be higher more than these ones. As shown in Fig. 1, mostly the ζ value increased with decreasing d . In addition, it was found that the ζ of PAN synthesized at center on the electrode, was higher than at the side.

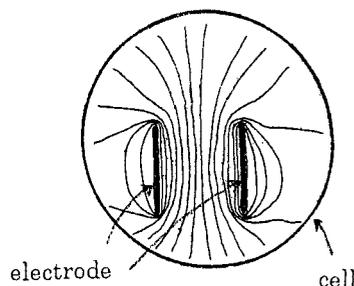


Fig.2 The electric field image in the electrolytic cell. Lines in the figure represent equipotential planes in two-dimension.

Figure 2 is an example showing a part of the equipotential lines in the cell drawn by the simulation on the conductive paper. The actual measurements of potentials for the simulation were carried out more minutely than shown in the figure. The electric field were estimated as the strength and the direction, separately. The direction of the electric field was represented by 'bending coefficient' δ . δ was defined as the tangent of the angle θ made between the electric field vector and the normal vector of the electrode surface. Where δ is zero, the equipotential plane is parallel to the electrode surface. Then, the δ and the strength E were

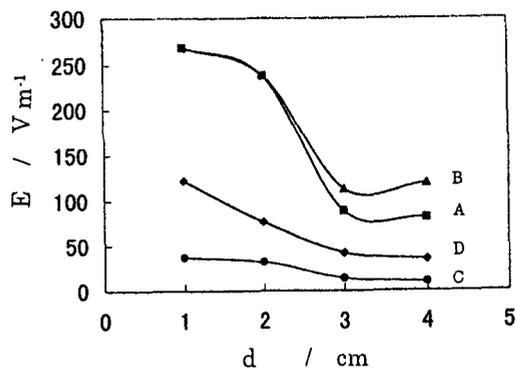


Fig.3 The plots of the strength E of the electric field around the position where PAN grew against electrodes distance d .

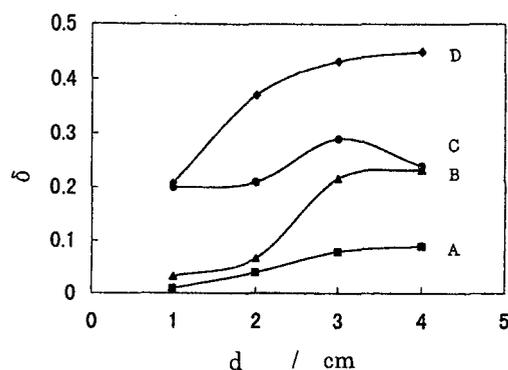


Fig.4 The plots of bending coefficient δ around the position where the PAN grew against electrodes distance d .

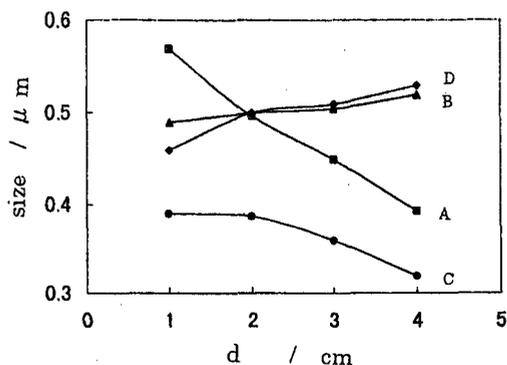


Fig.5 The plots of sizes of PAN 'yarn' against electrodes distance d .

plotted against d , respectively (Figs.3 and 4). In these figure, with increasing d , δ increased and E decreased. In addition, δ was large and E was small at side and rear surface of the electrode.

The relation between the sizes of PAN 'yarn' and d , shown in Fig.5, did not seem the same partly as that between the crystallinity and d . This discrepancy was considered to be come from that the bulky PAN yarns were not wholly crystalline and the crystals in the yarns were very small.

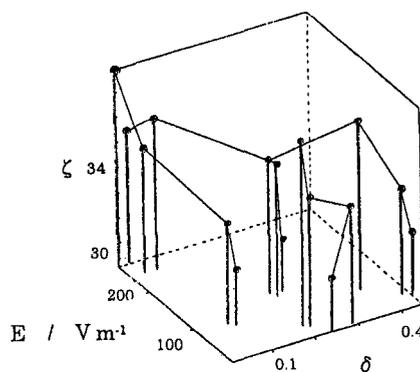


Fig.6 The three-dimensional plots of crystallinity ζ against the strength of electric field E and the bending coefficient δ around the position where the PAN grew.

These ζ , δ and E data were summarized in the three dimensional figure, Fig.6. From the results shown in this figure, it was found that the strong and vertical electric field to the electrode made the crystallinity high. It is possible to explain the effect of such two parameters on the crystallinity as follows. That is, the strong electric field may accelerate the reactant discharging at restricted position (zone) and the parallel equipotential plane to the electrode can make the product deposit onto the electrode surface directly and homogeneously. It is considered, therefore, the high crystalline PAN was obtained in the strong and vertical electric field to the electrode.

4. CONCLUSION

We investigated how the electric field influenced the aggregation of PAN synthesized electrochemically. The crystallinities of PANs were estimated and the electric fields in the electrolytic cell were simulated. Considering the relation of the crystallinities and the electric fields, it was found that the strong and vertical electric field around the working electrode exerted the effect on the control of high crystallinity of PAN.

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