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Author(s)	Onoda, Mitsuyoshi; Tada, Kazuya; Shinkuma, Akira
Citation	電気材料技術雑誌. 2005, 14(2), p. 71-74
Version Type	VoR
URL	https://hdl.handle.net/11094/76808
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Note	

電気材料技術雑誌 第14巻第2号
J.Soc.Elect.Mat.Eng. Vol.14, No.2, 2005

In Situ Polymerization Process of Polypyrrole Ultrathin Films

Mitsuyoshi Onoda[1,2], Kazuya Tada[1]

[1]*Graduate School of Engineering, University of Hyogo*
2167 Shosha, Himeji, Hyogo 671-2280, Japan
Phone/Fax: +81-792-67-4860, onoda@eng.u-hyogo.ac.jp

[2]*Department of Mechanical Engineering, Akashi National College of Technology*
679-3 Nishioka, Uozumi-cho, Akasi, Hyogo 674-8501, Japan

and

Akira Shinkuma

Kinden Corporation,
3-4 Honjo-Higashi, 2-chome, Kita-ku, Osaka 531-8550, Japan

In *in situ* polymerized pyrrole (PPy), the deposition process strongly depends on the nature of the substrate surface. That is, for a surface that is negatively charged, there is a linear correspondence between dipping time and the amount of PPy deposited on the substrate. However, in the case of a positively charged surface, there is an apparent rest period of approximately 10-20 min, during which no PPy is deposited. From optical absorption spectroscopy and photoelectron emission studies *etc.*, it became clear that oligomers of pyrrole were adsorbed on the positively charged surface during the rest period, as a result the polymerization reaction of PPy could proceed.

Recently, a new technique of constructing multilayer assemblies by consecutively alternating adsorption polyelectrolyte was developed. Rubner *et al.* have found that it is possible to extend this exciting new technique to the manipulation of conducting polymers.[1]

We have already reported that the nature of the substrate surface plays an important role in the early stages of the PPy growth process. That is, there is a linear correspondence between dipping time and the amount of PPy deposited onto the negatively charged substrate, however for surfaces that are positively charged, there is a rest period of 20-30 min during which no PPy is deposited. After this rest period, the growth of PPy on the surface is significantly less than that observed on a negatively charged surface. In particular, it is very interesting from fundamental and practical viewpoints to investigate what happened during the rest period.

In this paper, we discuss the initial deposition process of PPy onto the positively charged substrate.

1. Influence of the nature of the substrate surface

Figure 1 shows the growth of *in situ* polymerized PPy onto the negatively and positively charged surfaces as determined by monitoring the optical absorption of the as-grown film at 2.25 eV with time. It should be noted that the nature of the substrate surface plays an important role in the early stages of the PPy growth processes. That is, as we have already reported, the fact that PPy deposits in a very controlled manner on negatively charged surfaces makes it possible to use this process to fabricate monolayer and multilayer thin films with well defined layer thickness. Thus, when a substrate selectively patterned with regions that are negatively charged and regions that are positively charged is immersed into the PPy dipping solution for approximately 10-20 min, a thin conducting film of PPy will be deposited only onto the regions of the substrate that are negatively charged.

The monolayer deposition process as described here has been used to create extremely uniform films on negatively charged surfaces with superior adhesion. However, when PPy was deposited onto the positively charged surface, film adhesion and uniformity were observed to be significantly poor. That is, the basis of this *in situ* polymerization is the electrostatic attraction as mentioned above. Therefore, for the surface which is negatively charged, the PPy monolayer grows due to the electrostatic attraction developed between the SPS$^-$ polyanions and the delocalized positive charges (polarons and/or bipolarons) along the backbone of PPy. On the other hand, for the surface which is positively charged, the growth of the PPy film is quite difficult because the electrostatic repulsion developed between the TMS monolayer and the delocalized positive charges (polarons and/or bipolarons) along the backbone of PPy. However, as the rest period proceeded, the growth of the PPy film were observed and an almost linear relationship was recognized between dipping time and the absorbance of PPy as shown in Fig. 1. This result suggests that the nature of the positively charged surface changed the PPy film during this rest period and PPy became apt to polymerize.

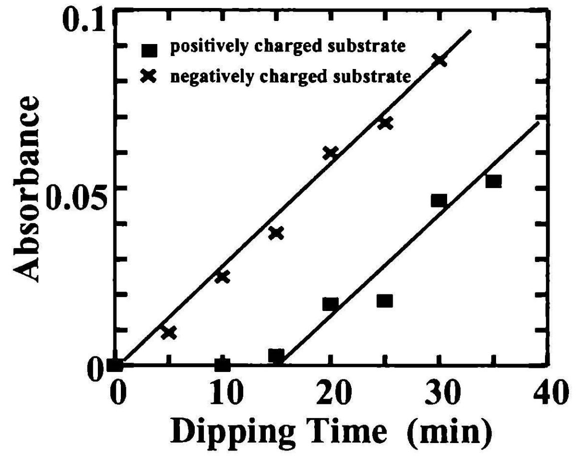


Fig. 1. Time dependence of the visible absorbance of in situ polymerized PPy deposited onto the negatively and positively charged surfaces.

2.Influence of the components in *in situ* polimerization electrolyte

It is also interesting from practical viewpoints to find what happens on the positively charged surface during rest time. By combing components of the *in situ* polymerization electrolyte, seven types of electrolyte, Py, *p*-TSNa, FeCl$_3$, Py+FeCl$_3$, Py+*p*-TSNa, FeCl$_3$+*p*-TSNa, and Py+*p*-TSNa+FeCl$_3$, were prepared and *in situ* polymerized PPy films were fabricated on the positively charged surface after the positively charge substrates were immersed into each electrolytes for 30 min. All electrolytes were the same concentration as that of the *in situ* polymerization electrolye and prepared at pH=1 using HCl. Each dipping solutions was aged for 30 min shielded from light and filtered using a 0.45 μm filter prior to use.

Figure 2 shows the relationship between the absorbance at 2.25 eV for *in situ* polymerized PPy after dipping in seven types of electrolyte solution for 30 min. There was no notable change in the rest period of the six types of electrolyte solution except for the Py+*p*-TSNa+FeCl$_3$ electrolyte. Accordingly, it is assumed that the adsorption of specific components of *in situ* polymerization electrolyte do not act as the polymerization process of PPy, but the polymerization reaction itself of PPy on the positively charged surface changes the nature of the substrate surface. However, in the case of Py+FeCl$_3$ electrolyte solution, the rest period appears regardless of the occurrence of a polymerization reaction. A detailed discussion can be find later.

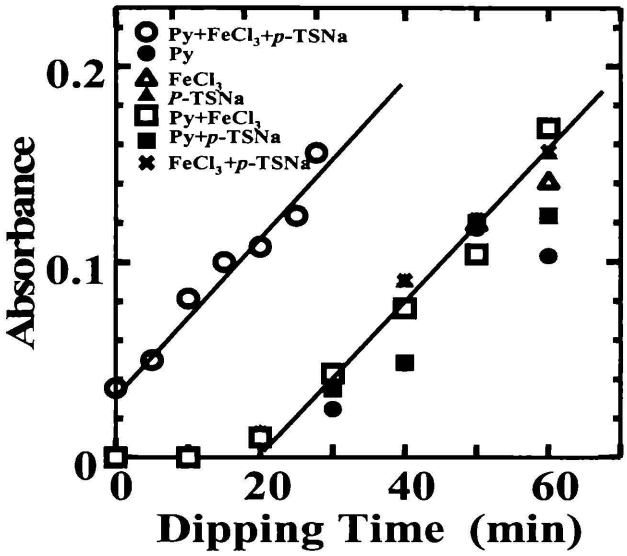
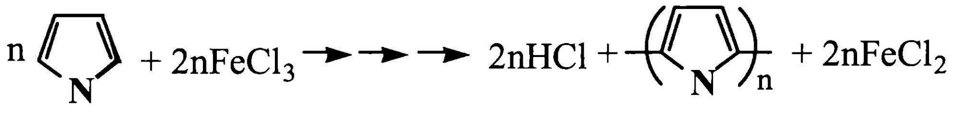


Figure 2. Relationship between the absorbance at 2.25 eV for *in situ* polymerized PPy after dipping in seven types of electrolyte solution for 30 minutes and the dipping time of solution

3. *in situ* polymerization in aqueous solution containing Py and FeCl$_3$

In the presence of FeCl$_3$ as an oxidizing agent, the polymerization reaction of Py proceeds as follows.



The following doping reaction also occurs at the same time.

$$2nFeCl_3 + e^- \longrightarrow nFeCl_4^- + nFeCl_2$$

Accordingly, there is no necessary *p*-TSNa for the polymerization of Py. However, as already described above, the rest period was observed at the early stage of the *in situ* deposition process of PPy using Py+FeCl$_3$ electrolyte solution. In this experiment, as the concentrations of Py and FeCl$_3$ are 0.04 mol/l and 0.005 mol/l, respectively, it is assumed that the concentration of FeCl$_3$ is quite low for the polymerization of Py.

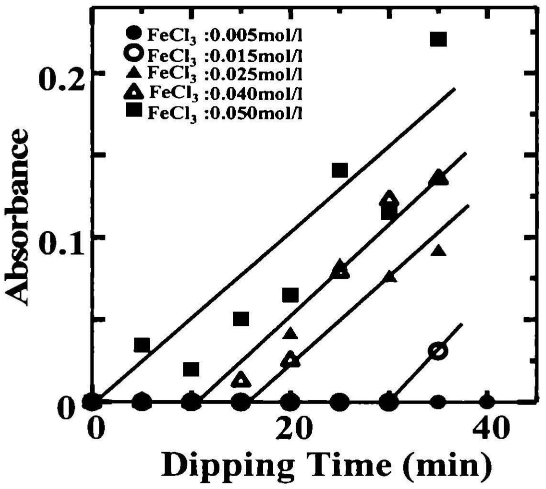


Figure 3. Dependence of the absorbance of *in situ* polymerized PPy on the positively charged substrate in Py+FeCl$_3$ electrolyte solutions on different FeCl$_3$ concentrations.

Figure 3 shows dependence of the absorbance of *in situ* polymerized PPy on the positively charged substrate in Py+$FeCl_3$ electrolyte solutions on the different $FeCl_3$ concentrations. The deposition process of PPy strongly depends on the concentration of $FeCl_3$. That is, with increasing $FeCl_3$ concentration, the rest period becomes shorter and disappears at a high concentration. In the case of an $FeCl_3$ concentration of 0.025 mol/l, the deposition process is almost the same as that of *in situ* polymerization electrolyte with regular concentration already shown in Figs. 18 and 19. This fact indicates that *p*-TSNa under *in situ* polymerization activates the oxidation ability of $FeCl_3$.

4. Conclusions

Multilayer thin film heterostructures comprised of alternating layers of PPV and SPAn were fabricated using a new self-assembly technique. We have obtained visible-light EL diode utilizing SPAn/PPV multilayer thin film. We had also demonstrated that polypyrrole, chemically produced by *in situ* oxidative polymerization, can be deposited as a highly uniform, ultrathin film onto a substrate with a high level of control over thickness. Furthermore, complex heterostructures can also be fabricated by simply alternating between solutions of conjugated and nonconjugated polyelectrolytes.

We have investigated the deposition process during a rest period which appeared on positively charged surface using optical spectroscopic methods such as optical absorption spectra and photoelectron emission studies. The result of the experimental study can be summarized as follows.

(1) For a surface that is positively charged, there is a rest period of approximately 10-20 min during which time no PPy is deposited.
(2) It is assumed that the adsorption of specific components of *in situ* polymerization electrolytes does not act as the polymerization process of PPy, but the polymerization reaction itself of PPy on the positively charged surface changes the nature of the substrate surface.
(3) Accompanying the polymerization reaction of Py occurring on the positively charged substrate during the rest period, oligomers of Py are formed and a suitable surface for the polymerization of Py is formed.
(4) *p*-TSNa under *in situ* polymerization activates the oxidation ability of $FeCl_3$.

References

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