Electrochemical Synthesis of Conducting Polypyrrole in Nucleophilic Solvent

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친핵성 용매하에서 전도성 Polypyrrole의 전기화학적 합성

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Abstract: Conductive polypyrrole films have been synthesized by electrochemical method in nucleophilic solvent such as N, N-dimethylformamide(DMF), dimethylsulfoxide(DMSO). The effect of protic acid as supporting electrolyte to decrease the nucleophilicity of the solvent was studied. Cyclic voltammetry, I-t transients were carried out to investigate the electrodeposition of conductive polypyrrole film on platinum electrode. Three peaks of 0.65V, 0.85V, and 1.2V vs. Ag/AgNO₃ indicated oxidation of monomer, oxidation of pyrrole to the platinum electrode and decomposition of polypyrrole film, respectively. With the I-t transients, nucleation process was confirmed and from obtained linear fits of I vs.t² resembles the metal film formation, and 2.15-2.26 of n-value could be calculated. As concentration of pyrrole or protic acid was increased, the conductivity of polypyrrole film increased linearly. Tensile strength and elongation were investigated for comparing the mechanical properties and also SEM was performed for morphology investigation.

요 약: N, N-dimethylformamide(DMF)와 dimethylsulfoxide(DMSO)와 같은 친핵성 용매에 protic acid인 p-toluenesulfonic acid 또는 benzenesulfonic acid를 지지전해질로 사용하여 전도성 polypyrrole 필름을 전해 합성하였다. Cyclic voltammogram을 통해 전기화학적 반응거동을 조사한 결과 0.65, 0.85, 1.12V vs. Ag/AgNO₃에서 모노머의 초기산화와 전극에서의 생성 모노머의 폴리머 성장, 그리고 약간의 분해에 해당되는 peak를 확인할 수 있었다. 전류-시간 곡선에서 전위가 증가하거나 pyrrole의 농도가 증가할 때 전류값이 증가함에 따라 nucleation에 의한 폴리머의 성장반응이라 추정하였다. 전류가 시간의 제곱에 직선성일 때 log(I/t²)과 전위와의 plot으로부터 n-value가 2.3정도임을 알았다. 전해중합시의 pyrrole 또는 protic acid의 농도가 증가함에 따라 생성 film의 전도도가 증가하였다. 인장강도와 연신율을 측정하여 기계적 물성을 검토하였으며 SEM을 이용하여 표면 morphology도 확인하였다.

1. Introduction

A hypothesis about organic polymeric compound known as a superior insulator was pronounced that conjugated double bonded polymer will be a semiconductor or conductor at room temperature by Little in 1964[1]. After that the metallic properties of polymeric $(SN)_x$ were synthesized by Walatka and Green in 1973 which become superconducting at low temperature under 0.3K[2-4]. Shirakawa and his co-workers synthesized polyacetylene(PA) using Al-Ti catalyst and contents of cis- and trans- could be controlled according to the temperature range[5-6]. They also reported that the conductivity of semiconducting PA film could be increased many orders of magnitude when doped with halogens or AsF_5[7]. But conducting PA film is easily oxidized in air and unstable to the heat.

Conducting polypyrrole was known to be stable at the temperature of plastic process and oxidized a little in air[8-13]. Also it could easily be synthesized by electrochemical method. Anodic formation of a polypyrrole black in aqueous sulfuric acid which has 8(ohm cm)$^{-1}$ of conductivity was reported in 1968 by Dall Olio. Diaz and his co-workers studied the anodic oxidation of pyrrole in acetonitrile (with 1% water) led to free-standing polypyrrole films which were highly conducting and could be easily lifted from the electrode surface. Most of the preparation of polypyrrole film, acetonitrile, THF, propylene carbonate were used for solvent containing $TEABF_4$, $TEAClO_4$ or $TEAPF_6$ for supporting electrolyte[14-17]. In nucleophilic solvent like DMF and DMSO solution, no film formation was reported[18]. In this experiment, the protic acid(p-toluenesulfonic acid, benzenesulfonic acid) were used to prepare the conductive polypyrrole film in DMF, DMSO electrolyte system. The relation of protic acid and pyrrole concentration for the formation of polypyrrole films were also studied. Also the conductivity and mechanical properties of each film were compared. Scanning electron microscope(SEM) was inspected in order to assure the morphology and cross sectional condition according to the conductivity of polypyrrole films.

2. Experimental

2. 1. Materials
P-toluenesulfonic acid, benzenesulfonic acid and pyrrole were used without further purification. N, N-dimethylformamide(DMF) and dimethyl sulfoxide (DMSO) were stirred with calcium hydride for one day, then distilled and stored over molecular sieves. All solutions were deoxigenated with a stream of argon gas within the cell prior to experiments.

2. 2. Instrumental Analysis
Cyclic voltammetry and current-time transients were carried out using a Potentiostat\Galvanostat (model 173, EG & G Princeton Applied Research Co) connecting to the cell with a Universal programmer(model 175) and X-Y-t recorder(model Vp-64, National). Short time responses were recorded by a IBM-AT computer and passed charge were measured on a digital Coulometer(model 179). To prevent the interruption of noise and irregular current, noise filter was set up between the reference electrode and the counter electrode. It was illustrated in Fig. 1. The experiments were all carried out in three electrode one compartment cell except constant current synthesis at 25℃. The working electrode was a Pt tip(area 0.4cm^2)sealed into a glass and the counter electrode was a Pt gauze. The electrode surface were heated in a flame, polished with activated alumina and washed with distilled water to remove contaminants and/or polymer caused from previous experiment.

The films were removed from the electrode surface and washed with solvent in a Soxhlet extractor for 1 hour and dried. The films for SEM were prepared as above passing 10mA/cm^2 current density and 15 coulomb of charge passed. For the conductivity measurement, four probe methods were performed with Regulated DC Power Supply(model ED-245B, ED Lab) connected to the Potable DC
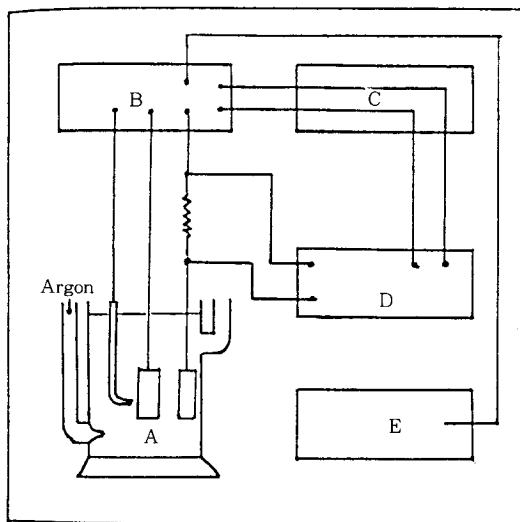
Fig. 1. Scheme of electrochemical measurement appa-
ratus.
A : Cell B : Potentiostat C : Function Genera-
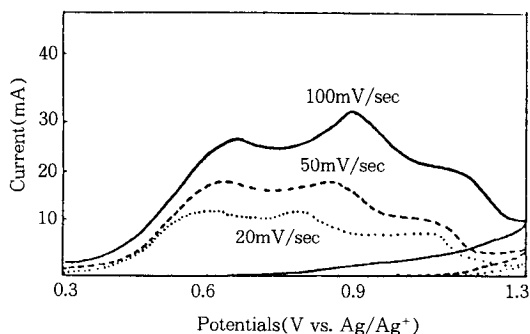tor D : X-Y-t Recorder E : Computer System

Fig. 2. Cyclic voltammogram of 0.05mol pyrrole on
Pt. electrode in DMF containing 0.5mol p-
TSA at scan rates of 100mV/sec; (---),
50mV/sec; (---), 20mV/sec; (···).

Potentiometer(Yokogawa Co. model 2727). Investi-
gation of morphology was carried out with SEM
(JSM 350 JEOL).

2. 3. Results and Discussion

The cyclic voltammogram for the electrochemical
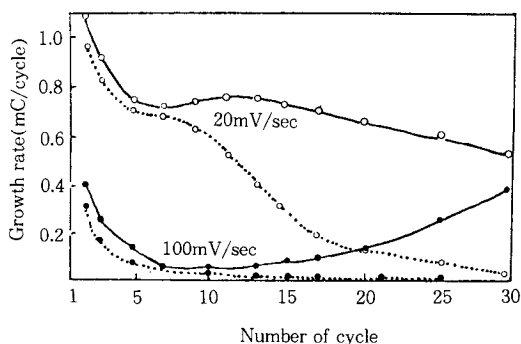oxidation of 0.05M pyrrole in N, N-dimethyl-

Fig. 3. Growth rate of polypyrrole films in different
system.
(—); DMF+TSA(0.5M)+Py(0.05M)
(···); DMF+BSA(0.5M)+Py(0.05M)

formamide and dimethylsulfoxide containing 0.5M p
-toluenesulfonic acid or benzenesulfonic acid as a
supporting electrolyte on a platinum electrode was
carried out to define its mechanism and is illustrat-
ed in Fig. 2. At least three peak potentials could be
seen, the first peak atq +0.65 V vs. $Ag/AgNO_3$ on
I-E curve indicated the potential of oxidation of
monomer. The second peak at +0.85 V corresponds
to the oxidation of pyrrole to the electrode surface.
And the further peak at most positive potential
near +1.2 V means that the decomposition of poly-
pyrrole involves lost conjugation or opening of pyr-
role ring in the polymer chain by nucleophilic attack
of solvent or anions. With the variation of the po-
tential scan rate(20, 50 and 100mV/sec), the peak
current showed linear with square root of scan rate.
This linearity led to diffusion controlled reaction.
These plots showed that the peak potential shifted
to the positive and peak current increased with the
increase of scan rate. At low scan rate the amount
of polypyrrole film formation was increased accord-
ing to long duration around higher oxidation poten-
tial than lower oxidation potential.

The growth rate of polypyrrole was illustrated in
Fig. 3. At 100mV/sec scan rate, the increase of
growth rate was observed after 13 cycles and had
no similarity with the increase at 20mV/sec. Be-

cause at high scan rate, the time of staying in decomposition potential was short and produced less amount of decomposited polypyrrole. There is no significance when synthesized with electrochemical method in DMF-benzenesulfonic acid. In DMSO/p-toluenesulfonic acid solution, only small amount had continuous decrease of growth rate.

The real area of electrode could be increased rapidly with high electronic conducting film and because of that more pyrrole could be oxidized. It has been assured that in each case the growth rate was increased with more than 0.3M pyrrole. The appearance and color resulted in the formation of polypyrrole on the surface might be seen by bare eyes. In DMF it was a thick black colored film but in DMSO thin yellow colored film.

A series of potential step experiments from +0.65V to +0.85V were carried out. Qualitatively different I-t responses were observed at various potentials. As shown in Fig. 4, with the potential increased only increased current correspond to the double layer charge was observed before 0.8V. Small peaks appeared over +0.8V of oxidation peak potential following increasing the current indicated the formation of monolayer and it moved at early stage with more positive potential. These peaks could explain that growth reactions of polymer by nucleation took place after the formation of modified layer on the electrode by dimerization14, 18). These types of behaviour have been described in metal deposition. This is also an indication that pyrrole oxidized more readily on polypyrrole than on platinum electrode because the formation of polypyrrole involves nucleation step [19]. In Fig. 5, the high concentration of pyrrole drove the increase of current. With low concentration only double-layer charge was observed. Because the high density of nuclei results in the peak of their overlap at an early stage, digital simulation was performed from 0 sec to 5.89 sec for the conformation and is illustrated in Fig. 6. It should be shown that after the formation of monolayer by a dimerization of radical cation, the polymer growth began. The des-
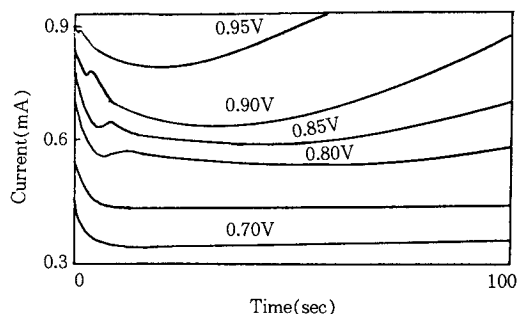

Fig. 4. I-t transients in response to potential step of 0.075mol pyrrole containing 0.5mol p-TSA in DMF on Pt. electrode.
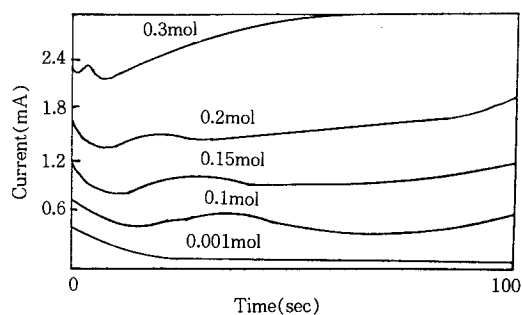

Fig. 5. I-t transients in response to 0.8V of Set potential at various concentration of pyrrole on Pt. electrode.
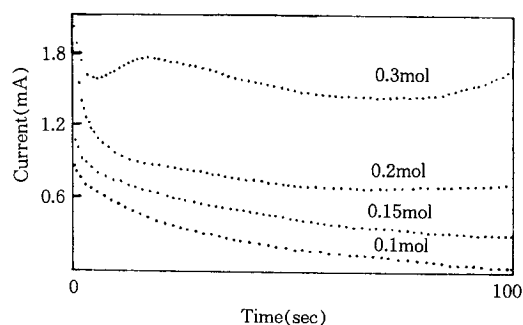

Fig. 6. I-t transients in response to 0.9V of Set potential at various concentration of pyrrole on Pt. electrode.

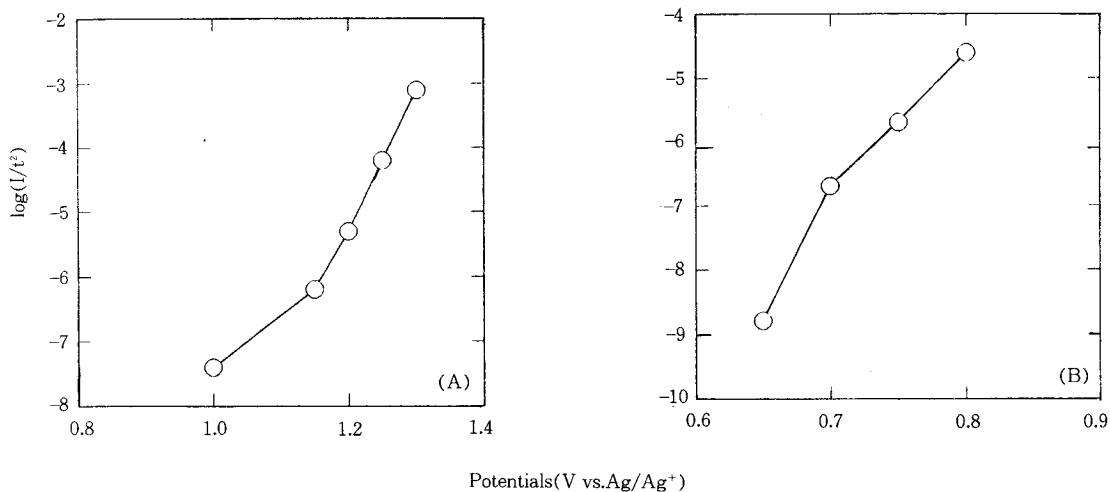ignation of the rising portion of the I-t curve, the rise became more rapid. The peaks became more

Potentials(V vs.Ag/Ag⁺)

Fig. 7. Plots of log(I/t²) vs. potential of 0.075mol pyrrole containing 0.5mol p-TSA in (A); DMF, (B); DMSO.

pronounced and the minima shift to shorter time scale as the potential is made more positive or as the concentration of pyrrole is increased. It was reported that if current I is equivalent to BK^3t^2, growth mechanism should be a 3-dimensional instantaneous nucleation or 2-dimensional progressive nucleation.

Correlation with a linear I-t² for the early rising part of the I-t curve consistent with an instantaneous nucleation/3-D growth mechanism. It is to be expected that n-value would calculated by following equation.

$$\frac{\log K}{E} = \frac{n\alpha F}{2.3RT}$$

E : constant
K : rate constant for electrón transfer
F : Faraday constant
n : electron per molecule redox
R : gas constant
T : absolute temperature

Corresponding to 8~12% of the total charge consumed for the deposition of the film and with the assumption that the formation of neutral film requires

2-electron pyrrole molecular, the degree of oxidation of the oxidized film could be estimated. A plot of $\log(I/t^2)$ vs. potential had a slope of $(47.46mV)^{-1}$ and n-value was 2.42. It is illustrated in Fig. 7. In DMSO solution, slope and n-value was 46.51 and 2.15, respectively. The n-value about 2.15-2.42 for the polymerization of pyrrole to oxidize film on platinum electrode indicates that approximately one anion for every four pyrrole units.

The conductivity of several films grown under different conditions is shown in Fig. 8. These films show an electrical conductivity at room temperature in the range of $0.1(ohm \; cm)^{-1} \sim 25(ohm \; cm)^{-1}$. Films were stable in air and showed little change after one month storage with the conductivity. It should be noted that there are four characteristic results from the comparison of conductivity. a): The conductivity was increased by increasing the concentration of pyrrole during electrochemical synthesis because higher concentration made the formation of layer fast. b): Similar results with the produced films as the concentration of protic acid is increased in the solution, because the protic acid might weaken the nucleophilicity of solvent. c): In DMF, it had higher conductivity of the produced
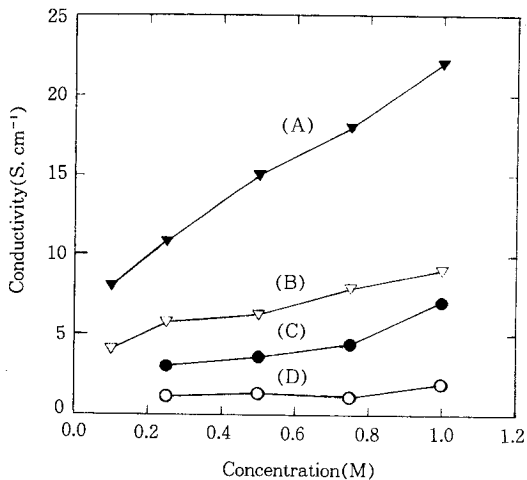
Fig. 8. Plots of conductivity vs. concentration of acid.
  (A) p–TSA+0.75M Pyrrole in DMF
  (B) p–TSA+0.5M Pyrrole in DMF
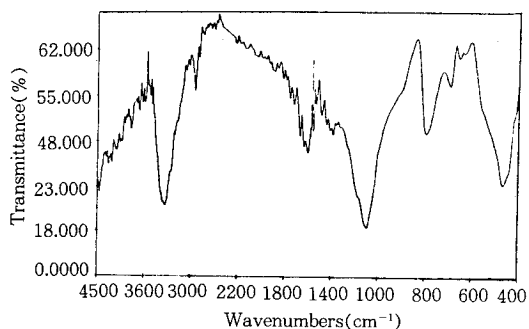 (C) BSA+0.75M Pyrrole in DMF
  (D) BSA+0.5M Pyrrole in DMF

Fig. 9. FT–IR spectrum of polypyrrole film intercalated with p–TSA.

Fig. 10. Plots of tensile strength and elongation vs. concentration of acid.
  (A) p–TSA+0.75M pyrrole in DMF
  (B) p–TSA+0.5M pyrrole in DMF
  (C) BSA+0.75M pyrrole in DMF

films than in DMSO, because solution conductivity of DMSO(3×10^{-6} Scm^{-1}) is lower than that of DMF (2×10^{-5} Scm^{-1}). d): P–toluenesulfonic acid showed significantly higher conductivity than benzenesulfonic acid used as supporting electrolyte for the formation of films because the pH value of p–toluenesulfonic acid is lower than that of benzenesulfonic acid.
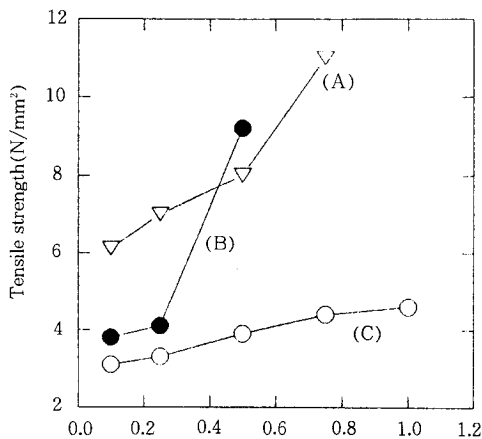
The characteristic peaks from FT–IR spectrum of conducting polypyrrole and tosylate was found and shown in Fig. 9. Tensile strength and elongation were investigated and illustrated in Fig. 10. There was higher tensile strength with the condition of
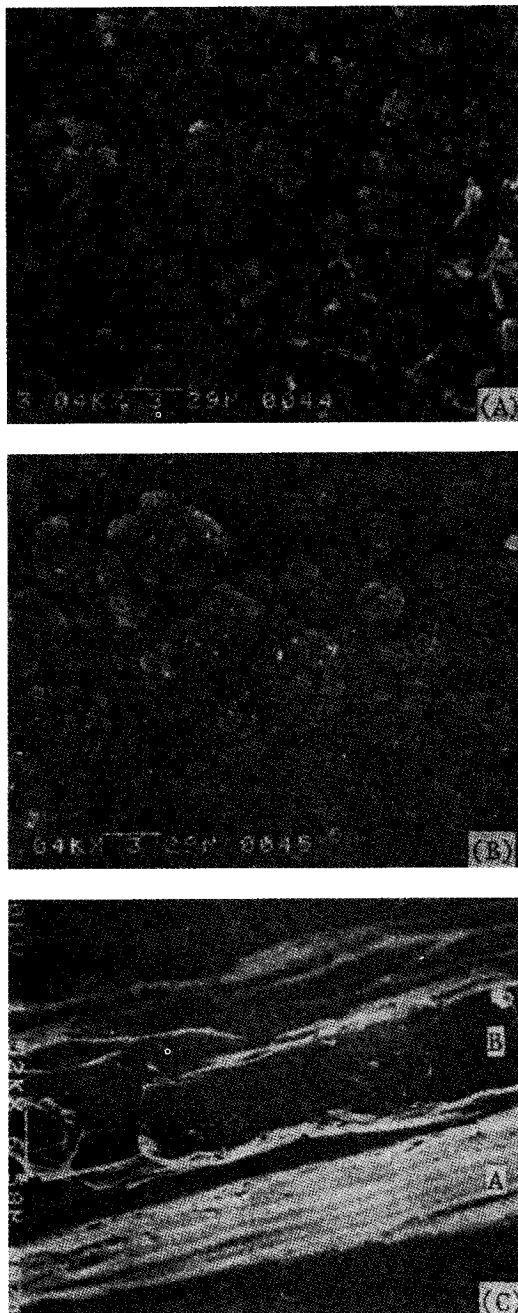
Fig. 11. SEM photographs of p-TSA and BSA inter-
calated in polypyrrole film facing the elec-
trolyte.
(A): DMF+p-TSA+pyrrole
(B): DMF+BSA+pyrrole
(C): Cross-section of polypyrrole film

0.5M pyrrole than 0.75M pyrrole. At low concentra-
tion, the number of monomer deposited on electrode
was smaller, and the polypyrrole grown compactly.
In order to compare the morpholgy, the conducting
polypyrrole films were analyzed by SEM. SEM pho-
tographs showed a rough surface of sponge hillocks
on the solution side and no evidence of fibrillar
structure could be found. As the films had higher
conductivity the polypyrrole grew more compactly.
By the cross-sectional photograph, the formation of
monolayer was assured.

3. Conclusion

The electrochemical oxidation of pyrrole in nu-
cleophilic solvent on a platinum electrode was per-
formed and the obtained results are as following.

1. Free-standing film of conducting polypyrrole
could synthesized by electrochemical method in
DMF, DMSO with protic acids.

2. Growth mechanism of polypyrrole was 3-D/in-
stantaneous nucleation.

3. When 15 Coulombs of charge were passed, the
polypyrrole film had shown 0.5-25 Scm^{-1} conductiv-
ity, 30-40um of thickness.

4. Calculated n-value was about 2.3.

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