

전기화학적으로 중합한 폴리아닐린의 전기적 성질

박연흠 · 조원호* · 미야타 세이조**

성균관대 섬유공학과 · *서울대 섬유공학과 · **동경 농공대 재료시스템공학과
(1988년 2월 24일 접수)

Electrical Properties of Electrochemically Polymerized Polyaniline

Yun Heum Park, Won Ho Jo*, and Seijo Miyata**

Department of Textile Engineering, Sung Kyun-Kwan Univ., Seoul, Korea

*Department of Textile Engineering, Seoul National Univ., Seoul, Korea

**Department of Material Systems Engineering, Tokyo Univ. of
Agriculture and Technology, Tokyo, Japan

(Received February 24, 1988)

요약 : 아닐린과 황산이 함유된 수용액에서 아닐린을 전기화학적으로 산화시켜 폴리아닐린 필름을 제조했으며 필름의 두께는 1미크론 정도였다. 필름표면은 피브릴 구조를 나타내었고 각 피브릴은 직경이 1000-2000 옴스트롬이었으며 임의의 방향으로 배향되어 있었다. 폴리아닐린 위에 프라즈마 중합된 폴리(*N,N'*-디페닐-*p*-페닐 렌디아민) (PDP) 박막과 금속(M) 막을 입혀 M/PDP/환원상태의 폴리아닐린(PA)/Au MIS 소자를 제조했다. Al/PDP/PA/Au 소자는 정류효과를 나타내었지만 Al/PDP/산화상태의 폴리아닐린/Au 소자는 옴기동을 나타내었다. 로그전기 전도도 대 $1/T$ 의 그래프로부터 활성화에너지 0.13eV를 얻었으며 $1/C^2$ 대 V의 그래프로부터 확산전위 3.37V, 전자 수용체 밀도 $2.25 \times 10^{19}/\text{cm}^3$ 및 공핍층폭 130 옴스트롬의 값을 얻었다.

Abstract : Polyaniline was prepared by electrochemical oxidation of aniline in aqueous solution containing aniline and sulfuric acid. The polyaniline films were about 1 micron thick. The film surface was composed of randomly oriented fibrils with diameter of 1000-2000 Å. The M/PDP/reduced polyaniline (PA)/Au MIS cells were fabricated by coating a thin plasma-polymerized poly(*N,N'*-diphenyl-*p*-phenylene diamine) (PDP) film on polyaniline and then a metal(M). The Al/PDP/PA/Au cell showed rectifying effect but the Al/PDP oxidized polyaniline/Au cell showed ohmic behavior. An activation energy of 0.13 eV was estimated from the plot of log conductivity versus $1/T$. A diffusion potential of 3.37V, an acceptor density of $2.25 \times 10^{19}/\text{cm}^3$, and a depletion layer width of 130 Å were estimated from the plot of $1/C^2$ versus V.

INTRODUCTION

Polyaniline was prepared by oxidizing aniline with KClO_3 or FeCl_3 as an oxidant.^{1,2} Recently, the electrochemical polymerization of aniline has been tested as a convenient synthetic procedure.³⁻¹¹ For the applications of electrochemically polymerized polyaniline, the electrode coating have received remarkable attention, since the electrodes with polymeric coatings show promise to electrocatalysis,^{12,13} antiphotocorrosion⁵ and analytical sensors.^{14,15}

Many workers have studied mainly on the electrochemical responses of electrochemically polymerized polyaniline in aqueous^{3-6,14,16,18,19} or nonaqueous^{8-10,16,17,20} electrolyte solutions.

In this work, the electrical properties of electrochemically polymerized polyaniline have been studied chiefly using the metal-semiconductor (MS) or the metal-insulator-semiconductor (MIS) cell in dry state.

EXPERIMENTAL

Electrochemical Polymerization

Polyaniline was prepared by electrochemical oxidation of aniline (reagent grade, Tokyo Kasei Co.) in aqueous solution containing 2 ml of aniline and 35 ml of 1M sulfuric acid in a 50 ml beaker. A gold film evaporated on a slide glass substrate was the cathode and a platinum plate (1.1 cm \times 1.1 cm \times 0.1 cm) was used as the anode. Polyaniline film was formed by electrolyzing aniline with a potentiostat (Npot 2501, Nikko CO.) at 1.2 V vs. a saturated calomel electrode (SCE) for 15 seconds at room temperature. The film thickness measured with an Onosokki digital liner gauge was around one micron. After the film formation, the gold electrode was rinsed with distilled water and then reduced at -1.8 V vs. SCE for 5 minutes in 0.03 N HCl solution (pH=1.5). The reduced polyaniline (PA) film was rinsed with distilled water and finally with methanol and immediately dried under vacuum for 24 hours.

Cell Fabrication

For the fabrication of MIS cell, dried PA was transferred into the plasma polymerization reactor without a mantle heater and an inner heater for heating the substrate in an earlier reactor.²¹ N,N'-diphenylene (DP) was plasma-polymerized in the cold system. The details of the plasma polymerization are reported by the authors in the previous paper.²¹ Finally aluminum or gold was evaporated on poly DP (PDP) film. The thickness of PDP film estimated from a bridge capacitance measurement using an impedance bridge (model 12K, Mita Musen Kenkyusho Ltd.) was around 80-100 Å. The configuration of Metal / PDP / PA / Metal MIS cell is shown in Fig. 1. The PDP layer is omitted in the fabrication of MS cell.

Electrical Measurements

Current-voltage characteristics were measured with an electrometer (TR-8641, Takeda Riken) and a DC voltage supply (Type 2553, Yokogawa Electrical Works, Ltd.) or a function generator (model FG-121B, NF Circuit Design Block Co., Ltd.). The voltage across the sample capacitor was slowly increased manually or automatically and the current was recorded with an X-Y recorder (model F-3F, Riken Denshi Co. Ltd.). The electrical conductivity was calculated from the tangent line passing through the origin in the I-V curve for Au / polyaniline / Au cells.

RESULTS AND DISCUSSION

For the investigation of the electrochemical responses of electrochemically polymerized polyaniline, the cyclic voltammogram of the polyaniline-

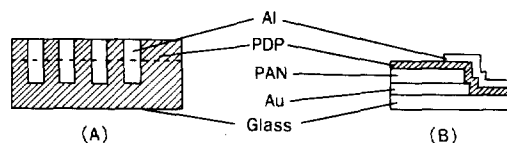


Fig. 1. Configuration of Al / PDP / PA / Au MIS cell, (A) : top view, (B) : side view.

coated gold electrode was measured in the range from -0.23 to +1.16 V vs. SCE and shown in Fig. 2. Two pairs of redox peaks (peaks A-A' and B-B') were observed, differing from the reported results⁵ in which one additional pair of redox peaks were observed. Reversible color change was observed as potential was scanned: from yellowish blue to dark green at 0.27V (peak A) and from dark green to yellowish blue at -0.1 V (peak A'). The color change persisted up to about one hundred potential cycles. After more than one hundred cycles, the film color turned gradually into dark greenish black and change little with potential. The shape of the voltammograms was deformed as the potential cycling was continued, i.e., both the redox peaks

A-A' and B-B' gradually decreased with an increase in the number of potential scans. The difference between the voltammograms shown in Fig. 2 and that reported previously⁵ may be due to the differences in the preparation conditions of the polyaniline films. In the present preparation, the electrode potential was kept at 1.2 V vs. SCE, while in the reported preparation, the oxidation of aniline was carried out at 0.9 V without the reference electrode.

Fig. 3 shows the electrical conductivity versus the dedoping (reducing) time. A conductivity of about 10^{-3} S/cm at the initial oxidized state decreased to a limiting value of 2.5×10^{-5} S/cm after electrochemical dedoping for 100 seconds. This result suggests that the conductivity of the polyaniline film can be controlled by the dedoping (reducing) time.

In the polyaniline SEM micrograph (Fig. 4-a) there was no sign of powder which was found by Diaz et al.⁶ On the other hand, the porous and fibrillar structure is very similar to that of polyacetylene.²² Polyaniline film consists of randomly oriented fibrils with diameters of 1,000-2,000 Å which is 5-10 times larger than those of polyacetylene fibrils, while the insulating PDP film for the protection coating of polyaniline surface is very smooth and pinhole-free as shown in Fig. 4(b).

Fig. 5 shows a current density-voltage relationship of Al/PDP/Oxidized polyaniline/Au cell. The response is symmetrical and shows an ohmic contact between aluminum and oxidized polyaniline (the contact between gold and oxidized polyaniline is also ohmic). On the other hand, Fig. 6 shows a current density-voltage response of Al/PDP/PA/Au cell. The asymmetrical response shows a nonohmic or rectifying contact. The disparity in current density-voltage characteristics between oxidized and reduced polyaniline films is explained by means of the following equations²³:

$$\Phi_b = E_g - (\Phi_m - X_s) \tag{1}$$

$$X_s = \Phi_s + (E_v - E_F) - E_g \tag{2}$$

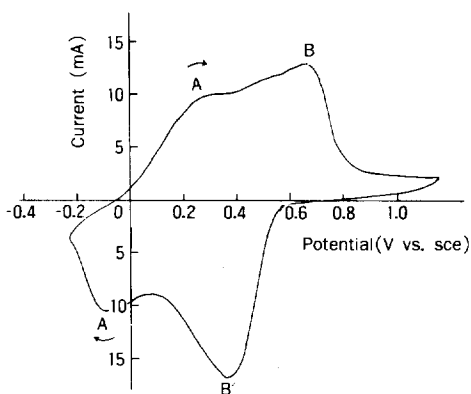


Fig. 2. Cyclic voltammogram of the polyaniline-coated gold electrode in 0.03 N HCl ($f=0.01$ Hz).

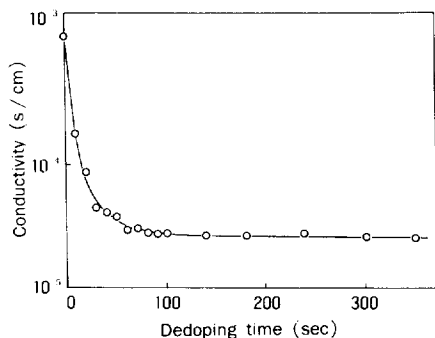


Fig. 3. The electrical conductivity vs. the dedoping time for polyaniline.

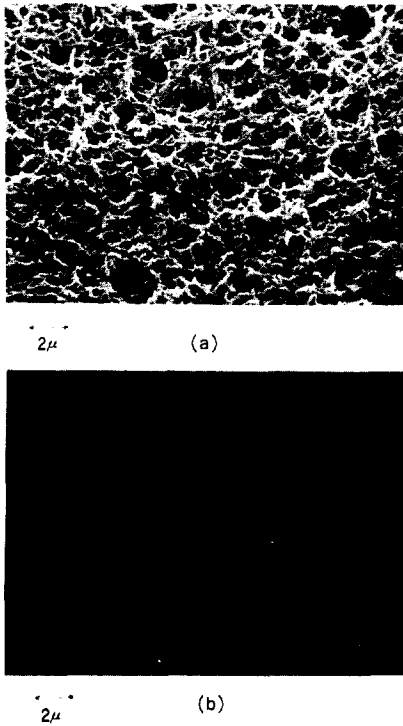


Fig. 4. SEM photographs of polyaniline (a) and PDP (b) films (X4500).

where X_s , E_v , and E_F are the electron affinity, the energy level of valence band, and Fermi level of a semiconductor (polyaniline), respectively. From equations (1) and (2), equation (3) is obtained,

$$\Phi_b = (\Phi_s - \Phi_m) + (E_v - E_F) \quad (3)$$

By the acceptor dopant contained in oxidized polyaniline, the Fermi level shifts toward the valence band and the value of $E_v - E_F$ becomes smaller, resulting in the decrease of the barrier height Φ_b . Therefore the Al/PDP/oxidized polyaniline/Au cell shows an ohmic behavior and the Al/PDP/PA/Au cell shows a Schottky barrier.

Fig. 7 shows a semilogarithmic plot of the current density versus the forward bias voltage for an Al/PDP/PA/Au cell. The forward bias corresponds to a negative voltage at the aluminum electrode with respect to the gold electrode, therefore

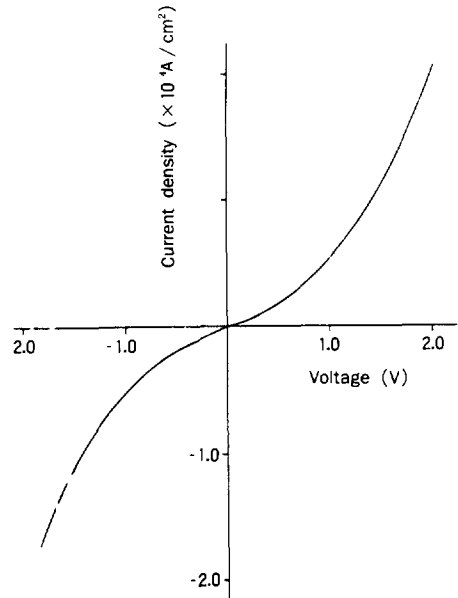


Fig. 5. Current density-voltage characteristic for Al/PDP/oxidized polyaniline/Au cell.

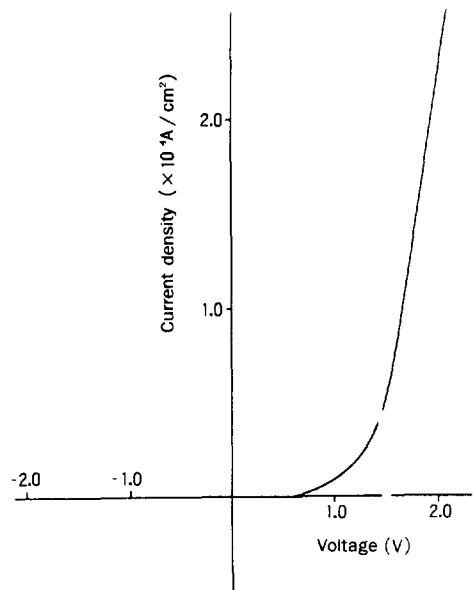


Fig. 6. Current density-voltage characteristic for Al/PDP/PA/Au cell.

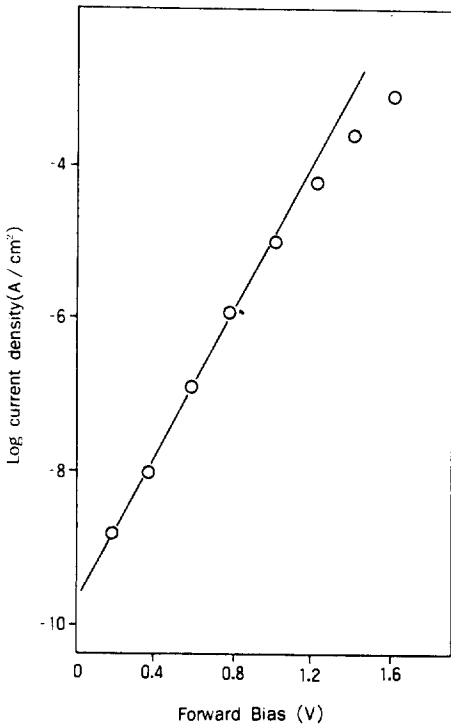


Fig. 7. Log current density vs. forward bias voltage for Al/PDP/PA/Au cell.

the electrons were transferred from the aluminum electrode to p-type polyaniline. A linear dependence was given upto 1.0 V. A slight deviation was observed at higher voltages. To describe the Schottky barrier in the dark, the ideality factor n was calculated to be 3.0 from the slope of the straight line. This value is higher than the values for the inorganic semiconductors such as Si ($n=1.02$) and GaAs ($n=1.04$).²⁴ The high value of n might be due to the residual dopant in the depletion layer and bulk of PA. The SO_4^{2-} can create additional energy levels in the band gap of PA to which electrons can transfer from the filled valence band, leaving holes behind. The holes may tunnel from the valence band of PA to the aluminum conduction band through the thin insulating PDP film. This tunneling is enhanced by additional energy levels in the depletion layer and is responsible for the high

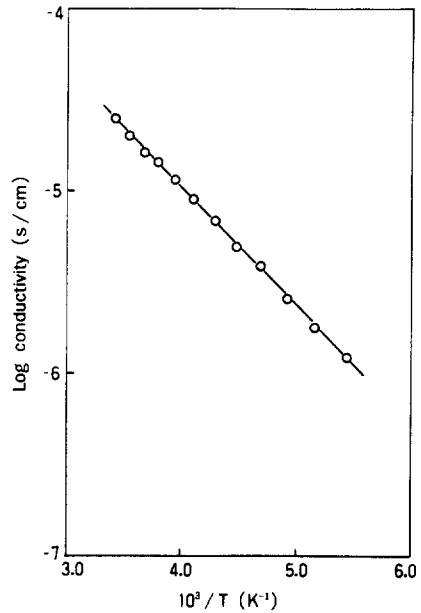


Fig. 8. Log conductivity vs. $1/T$ for reduced polyaniline at 2.0 V.

value of the diode ideality.

Fig. 8 shows the temperature dependence of the electrical conductivity of PA. As temperature decreased, the conductivity dropped from 2.5×10^{-5} S/cm at room temperature to 1.2×10^{-6} S/cm at 183.5°K. A plot of log conductivity versus $1/T$ gave a straight line fit in the range. The activation energy was 0.13 eV.

Fig. 9 shows the current-voltage trace of Al/PA/Au cell. It was recorded by applying a triangular voltage signal to the aluminum electrode at 0.1 Hz. The amplitude of applied voltage V_0 was 1.2 V. A vertical line drawn at any voltage along the horizontal axis intersects the current-voltage trace at two points. The distance between the intersections gives a value of $i_+ - i_-$ at voltage V . Inspection of Fig. 9 with Eq.(4),²⁶ where f is the frequency, indicates that the capacitance C is voltage dependent.

$$C = (i_+ - i_-) / 8V_0 f \tag{4}$$

The plot of $1/C^2$ versus V evaluated from the trace in Fig. 9 is shown in Fig. 10. The ideal

linear relationship between $1/C^2$ and V is seen here, which implies the presence of depletion layer in PA. Using Eq. (5)²⁵ the diffusion potential was evaluated to be 3.37 V from the intersection of straight line with horizontal axis in the $1/C^2$ vs. V plot. A derived value of the acceptor density, N_d from the slope of straight line was $2.25 \times 10^{19} \text{ cm}^{-3}$.

$$1/C^2 = 2(\Phi_0 + V) / q\epsilon\epsilon_0 N_d A^2 \quad (5)$$

Using Eq. (6),²⁶ the depletion layer width W was calculated to be 130 \AA .

$$W = (2\epsilon\epsilon_0(\Phi_0 + V) / q N_d)^{1/2} \quad (6)$$

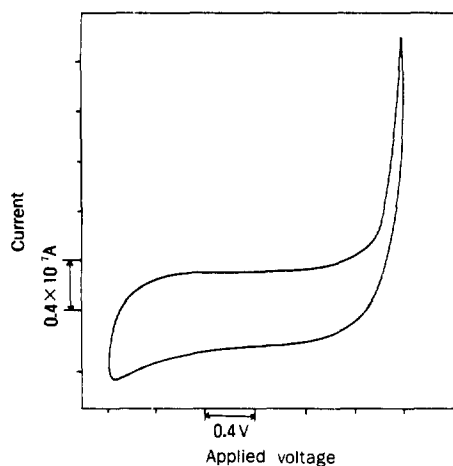


Fig. 9. Dark current-voltage trace for Al/PA/Au cell.

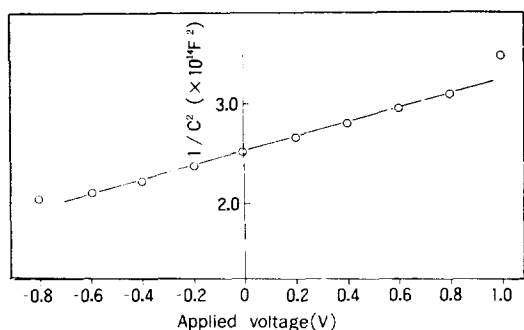


Fig. 10. Relationship between capacitance and applied bias to Al electrode for Al/PA/Au cell.

These results indicate that the present diode has the lower value of W and the higher values of Φ_0 and N_d compared with the inorganic Schottky diode.²⁵

CONCLUSION

From the results of the surface analysis, electrochemical responses, electrical characteristics of electrochemically polymerized polyaniline, the following conclusion can be drawn:

- 1) The film surface exhibits a fibrillar structure with randomly oriented fibrils of diameter about 1000-2000 \AA .
- 2) The cyclic voltammogram shows two pairs of redox peaks. This result is different from the previously reported work by Noufi et al.⁵ in which one additional pair of redox peaks were observed. The disagreement between the reported work and the present investigation can not be explained clearly, but it might be due to the differences in the polyaniline preparation conditions.
- 3) The current density-voltage characteristic for the Al/PDP/PA/Au cell shows a rectifying behavior but that for Al/PDP/oxidized polyaniline/Au cell shows the ohmic behavior.
- 4) The ideality factor is calculated to be 3.0 from a plot of the log current density and the forward bias voltage for the Al/PDP/PA/Au cell.
- 5) An activation energy of 0.13 eV is estimated from the plot of log conductivity versus temperature.
- 6) A diffusion potential of 3.37 V, an acceptor density of $2.25 \times 10^{19} / \text{cm}^3$, and a depletion layer width of 130 \AA are estimated from the plot of $1/C^2$ versus V .

REFERENCES

1. J. Langer, *Solid State Comm.*, **26**, 839(1978).
2. A. Bingham and B. Ellis, *J. Polym. Sci.:Part A-1*, **7**, 3229(1969).
3. D. M. Mohilner, R. N. Adams, and W. J. Argersinger, Jr., *J. Am. Chem. Soc.*, **84**, 3618 (1962).

4. J. Bacon and R. N. Adams, *J. Am. Chem. Soc.*, **90**, 6596(1968).
5. R. Noufi, A. J. Nozik, J. White, and L. F. Warren, *J. Electrochem. Soc.*, **129**, 2261(1982).
6. A. F. Diaz and J. A. Logan, *J. Electroanal. Chem.*, **111**, 111(1980).
7. J. J. Langer, *Materials Sci.*, **10**(1-2), (1984).
8. S. Wawzonek and T. W. McIntyre, *J. Electrochem. Soc.:Electrochem. Sci.*, **114**, 1025(1967).
9. R. L. Hand and R. F. Nelson, *J. Am. Chem. Soc.*, **96**, 850(1974).
10. G. Mengoli, M. T. Munari, P. Bianco, and M. M. Musiani, *J. Appl. Polym. Sci.*, **26**, 4247 (1981).
11. M. Breitenbach and K. H. Heckner, *Electroanalytical Chem.*, **43**, 267(1973).
12. N. Oyama and F. C. Anson, *Anal. Chem.*, **52**, 1192(1980).
13. N. Oyama, K. Sato, and H. Matsuda, *J. Electroanal. Chem.*, **115**, 149(1980).
14. T. Kobayashi, H. Yoneyama, and H. Tamura, *J. Electroanal. Chem.* **161**, 419(1984).
15. W. R. Heineman, H. J. Wieck and A. M. Yacynych, *Anal. Chem.*, **52**, 345(1980).
16. T. Ohsaka, Y. Ohnuki, N. Oyama, G. Katagiri, and K. Kamisako, *J. Electroanal. Chem.*, **161**, 399(1984).
17. Y. Ohnuki, H. Matsuda, T. Ohsaka, and N. Oyama, *J. Electroanal. Chem.*, **158**, 55(1983).
18. B. Aurian-Blajeni, I. Taniguchi, and J. O' M. Bockris, *J. Electroanal. Chem.*, **149**, 291 (1983).
19. N. Oyama, Y. Ohnuki, K. Chiba, and T. Ohsaka, *Chem. Soc. of Japan, Chem. Lett.*, 1759(1983).
20. A. Bolkov, G. Tourillon, P. C. Lacaze, and J. E. Dubois, *J. Electroanal. Chem.*, **115**, 279 (1980).
21. Y. H. Park, H. Tsutsumi, S. Tasaka, and S. Miyata, *Polymer J.*, **18**, 713(1986).
22. J. Mort and G. Pfister, "Electronic Property of Polymers", Wiley -Interscience, New York, p273, 1982.
23. J. Kanicki, "Handbook of Conducting Polymers", vol. 1, T. A. Skotheim, Ed. Marcel Dekker, New York, p571, 1986.
24. E. S. Yang, "Fundamentals of Semiconductor Devices", McGraw-Hill, New York, p132, 1978.
25. *Ibid.*, p126-127.
26. A. J. Twarowski and A. C. Albrecht, *J. Chem. Phys.*, **70**, 2255(1979).