Transactions of the Materials Research Society of Japan 29 [3] 767-769 (2004)

Enhanced Electrochemomechanical Deformation of Polyaniline Film by Optimization of pH and Electrolyte Concentration

Wataru Takashima, Megumi Nakashima*, Shyam S. Pandey and Keiichi Kaneto
Graduate School of Life Science and Systems Engineering (LSSE), Kyushu Institute of Technology,
2-4 Hibikino, Wakamatsu-ku, Kitakyushu, Fukuoka 808-0196, Japan
Fax: 81-93-695-6012, e-mail: takashima@life.kyutech.ac.jp
*Department of Computer Science and Systems Engineering, Kyushu Institute of Technology,
680-4 Kawazu, Iizuka, Fukuoka 820-8502, Japan

pH dependences of electrochemomechanical deformation (ECMD) with cyclic voltammetry (CV) have been investigated in conducting polymer, polyaniline (PANI). In the electrolytes equilibrated with 1M HCl and 1M NaOH (1M HCl/NaOH), the film exhibited the deformation of 4.2% at pH 1.5, which indicates the enhancement of ECMD magnitude of 27% from that obtained at pH 0.5 (3.3%). In the case of electrolytes equilibrated by mixing 1M HCl with 1M NaCl, it was found to show the enhancement of ECMD magnitudes of 6.2% at pH 1.5, indicating 88% increase of ECMD magnitude from that at pH 0.5. pH region having the large ECMD magnitude tends to expand toward the higher pH region with the increase of chloride concentration. The maximum of ECMD magnitude was finally reached to be around 6.7% at pH 2 in 3M HCl/NaCl. The redox charge collected from CV curves tends to show the increase as a function of chloride concentrations at pH > 1.5, indicating that the film was electrochemically activated with the chloride ions. The results can be explained by the enhancement of protonation in relatively high pH region supported by Donnan effect.

Key words: Electrochemomechanical Deformation, Polyaniline, pH dependence, Soft Actuator, Donnan effect

1. INTRODUCTION

In the area of the industrial development of biomimetic devices and humanoid robotics, the large progresses have been achieved in the recent past. The development of soft actuator having the high performance is an important requirement towards the fabrication of artificial muscles. Electrochemomechanical deformation (ECMD) which is one of the intrinsic characteristics of conducting polymers has received a good deal of attentions in the area of biomimetics due to its superior force generation reaching over several MPa.[1] However, the deformation magnitude within several % [2,3] is still small for the practical usage. For the purpose to enhance the deformation magnitude, variety approaches have been conducted by many researchers. [4-6]

Conducting polymer, polyaniline (PANI), is one of the materials having good technological potential for soft actuator fabrication because of its processibility to cast into the freestanding film from N-methyl-2-pyrrolidone (NMP) solutions. However, the electrochemical activity limited in low pH region is the stumble block for the practical usage.[3,7] The maximal ECMD magnitudes were also reported to be around 4-5% attained only in the solution having PF_6^- anion.[2] Therefore, it is worthwhile to develop the way for expanding the electroactive region toward higher pH in PANI system, especially with smaller Cl^- anion.

This paper reports that the optimization of electrolyte could successfully expand the electrochemomechanical activity of PANI towards the relatively high pH regions.[8] It was found that the ECMD magnitudes were also enhanced from 3.3% at pH 0.5 to 6.7% at pH 2 in 3M HCl equilibrated with 3M NaCl.

2. EXPERIMENTAL

PANI was synthesized by chemical oxidation of aniline monomer with ammonium peroxodisulfate described previously.[9] The obtained polyaniline powder was dried and dedoped into the emeraldine base (EB) state. N-methyl-2-pyrrolidone (NMP) solution was prepared as 3 wt% for casting the freestanding EB film. A strip form having 4-6 mm as length, 1.4-1.8mm as width and 12-18_m as thickness was employed as the sample for ECMD evaluation. Protonation was carried out in 1M HCl during 3-5 min sonication before to use. The film conductivity was obtained to be 5 S/cm.

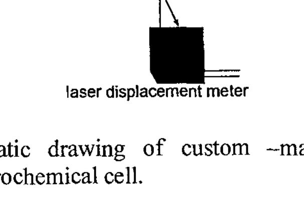

Fig.1 Schematic drawing of custom –made double jacketed electrochemical cell.

Direct measurement system of ECMD behavior with cyclic voltammetry (CV) was employed.[7,10] A double jacketed glass tube was used for electrochemical cell as shown in Fig.1. Julabo F25-MP was used as temperature controller by circulating the water in the jacket. The relationship between the sample and the controller temperatures was used for the calibration. Ag/AgCl was prepared from 0.7mm Ag wire in 0.1M HCl polarized anodically during 1h. Ag/AgCl and Pt were used as reference and counter electrodes, respectively. CV measurements were performed with potentio/galvanostat (Hokuto Denko HA-501) and function generator (Hokuto Denko HB-105). A sweep speed of 5mV/s was employed for CV measurements. The data for ECMD and CV curves were collected in the range from −200 to 550mV vs Ag/AgCl. ECMD and CV curves were preliminary measured in 1M HCl solution for 10 CV cycles, followed by the measurement at various pH. [7,10]

Electrolytes were prepared from HCl mixing with NaCl (abbreviated into HCl/NaCl here and after) having the same concentration equilibrated at a certain pH. For comparison to those systems, equilibrated electrolytes mixed with HCl and NaOH having the same concentration (abbreviated into HCl/NaOH here and after) were also used as for the control experiment. It should be noted that for HCl/NaCl solutions, the electrolyte concentration should be defined in a certain molar value for anion (viz., Cl^- in this study) and pH for cation concentrations, respectively. Meanwhile, HCl/NaOH solutions define only the proton concentration as pH value. [8]

3. RESULTS AND DISCUSSION

3.1 pH dependence of ECMD characteristics

In HCl/NaOH solutions, obtained ECMD magnitude was found to be 3.2% at pH 0.3. With increase of pH, ECMD magnitude was monotonically increased up to 4.3% at pH 1.5 as the maximum (Fig.2(a)). At pH >1.5, ECMD magnitude turned to decrease and was to be around 1.8% at pH 3.0. The results indicate that the ECMD enhancement was to be around 25% in HCl/NaOH solutions.

In the case of 1M HCl/NaCl, further strong pH dependence appeared as shown in Fig.2(b). ECMD magnitude was drastically increased from 3.2% to 6.2% as a function of pH from 0.5 to 1.5. At around pH 1.5 ECMD magnitude exhibited a maximum then turned to decrease as a function of pH. Even at relatively large pH region of 3.0, ECMD magnitude still conserved to be 3.4%, which is almost the same magnitude obtained at pH 0.5. The results can be expressed as the enhancement of EDMD behaviors by employing the concentrated chloride.

The comparison of the results between HCl/NaOH and HCl/NaCl indicates the anion concentration plays an important role for the increase of ECMD magnitude. Increase of a certain chloride concentration will promote the magnitude of ECMD behavior. The anodic expansion during CV measurement can be explained by the anion insertion. Therefore, the high concentration of chloride will increase the anodic expansion during redox process. The increase of pH depresses the proton exchange because of proton dilution. It follows the promotion of anion exchange, alternatively. As the result, the anodic expansion seems to increase as compared to the cathodic expansion caused by the proton injection.

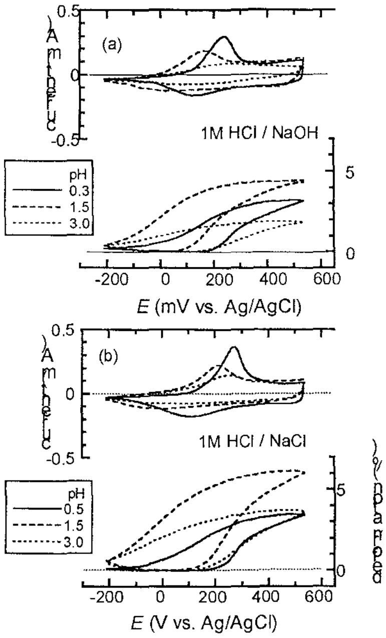

Fig.2 pH dependent ECMD curves with CV measurements of a freestanding PANI film prepared with (a) 1M HCl and NaOH, and (b) 1M HCl and NaCl.

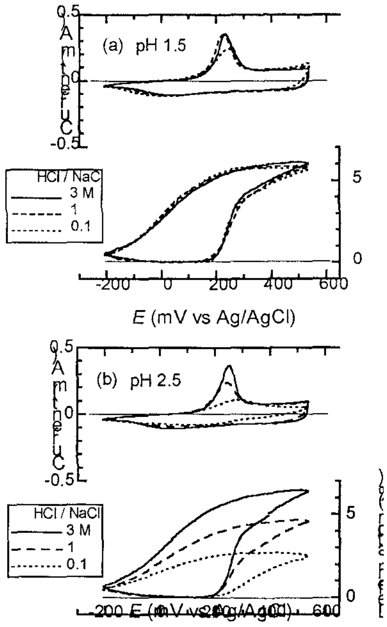

Fig.3 ECMD curves with CV measurements in various electrolyte concentrations at (a) pH 1.5 and (b) pH 2.5. All electrolytes were equilibrated with HCl and NaCl solutions in both having the same concentration.

3.2 Concentration dependence of ECMD characteristics

Figures 3 (a) and (b) show the concentration dependence of ECMD curves with CV measurements at pH 1.5 and 2.5, respectively. The similar large magnitudes were observed for all electrolyte concentrations at pH 1.5. In the case of higher pH region, pH grater than 1.5, ECMD behaviors varied with the electrolyte concentrations. Typical result was shown in Fig. 3(b) at pH 2.5. ECMD magnitude tends to decrease with the dilution of electrolyte. It is interesting to note that at low pH region, i.e. pH less than 1.5, the half redox potential exhibited the Nernstian characteristics having –60mV/pH as slope. This negative slope can be associated to the characteristics as proton-controlled region. [8]

At higher pH region i.e. pH greater than 1.5, however, the pH dependence of redox potential was not observed. It should be noted that the redox charge collected CV curve tends to show the concentration dependence at pH > 1.5, which indicates that the redox activities also change with the chloride concentration in this range (Fig.4). Therefore, the region of pH > 1.5 might be a kind of anion (chloride ion in this case) controlled region. It should be noted that ECMD magnitudes were attained to be 5% at pH 1.5 in the presence of a small quantity of NaCl (0.05M), which is still large magnitude as compared to that without NaCl as shown in Fig.2(a). Furthermore, even at pH 2.5, ECMD magnitude stayed over 6% in 3M HCl/NaCl. The results indicate that the presence of NaCl well contributes for the enhancement of ECMD magnitude particularly in the higher pH regions.

3.2 Concentration effect on redox charge

Figure 4 shows the pH dependence of redox charge normalized by film volume (Q_{red}/V) at various electrolyte concentrations. This relationship also divides the pH dependence into two zones. At pH < 1.5, Q_{red}/V tends to increase as a function of pH, which is independent from the electrolyte concentration similarly with that of ECMD magnitude (Fig.3(a)). The increase of Q_{red}/V can be explained by the shift of half-redox potential towards the negative polarity. Even in the shift of redox peak, the potential windows were fixed for all CV, which indicates that for PANI the oxidation/reduction levels were changed with pH. It should be noted that PANI possesses a couple of redox reactions.[7] Therefore, for the large shift of half-redox potential as a function of pH, reactions from emeraldine salt (ES) to pernigraniline salt (PS) state would be incorporated. This might affect the ECMD behaviors.

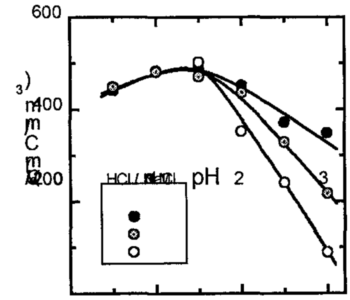

Fig.4 pH dependence of redox charge (Q_{red}) normalized to the unit volume in various concentrations of electrolyte

In the case at pH > 1.5, Q_{red}/V strongly depends upon the electrolyte concentrations. This also well corresponds with the pH dependence of ECMD magnitude as shown in Fig. 3(b). The decrease of Q_{red}/V in this pH region can be expressed as decrease of dopoing, viz., deprotonation of PANI. Taking the fact that the increase of electrolyte maintains relatively large Q_{red}/V into account, the concentration of electrolyte well contributes for the increase of electroactivation for PANI in this pH region. This phenomenon can be explained by considering the *Donnan effect*. The effect of electrolyte strength upon the protonation of PANI has been discussed by many research groups taking the Donnan potential into consideration.[11-14] The redox charge, Q_{red}, collected from CV curves renders the redox activities of the film, which might be associated with the degree of protonation. Fig.4 shows the obtained pH dependence of Q_{red} at various concentrations. The enhancement of ECMD magnitude discussed in this study can be expressed as one of the good example for the exploitation of Donnan effect into the electrochemical device.

4. CONCLUSION

pH dependence of electrochemomechanical deformation (ECMD) in polyaniline (PANI) film was investigated at various electrolyte strengths. It was found that at pH < 1.5, the film exhibited the monotonic decrease of ECMD magnitude as a function of pH. In this pH region, ECMD magnitude varied with the electrolyte concentrations. The increase of concentration well enhances the ECMD performance in terms of deformation magnitude and electroactive pH region without bulky anion. The observed enhancement of ECMD magnitudes can be explained as the result of Donnan effect of PANI.

Authors express their thanks to Eamex Co., for financial support.

REFERENCES

[1] Y. Sonoda, W. Takashima and K. Kaneto, *Synth. Met.*, **119**, 267-268 (2001).

[2] K. Kaneto and M. Kaneko, *Appl. Biochem. Biotechnol.*, **96**, 13-23 (2001).

[3] K. Kaneto, Y. Sonoda and W. Takashima, *Jpn. J. Appl. Phys.*, **39**, 5918-5922 (2000).

[4] L. Bay, K. West and S. Skaarup, *Polym.*, **43**, 3527-3532 (2002).

[5] L. Bay, K. West, P. Sommer-Larsen, S. Skaarup and M. Benslimane, *Adv. Mater.*, **15**, 310-313 (2003).

[6] S. Hara, T. Zama, S. Sewa, W. Takashima and K. Kaneto, *Chem. Lett.*, **32**, 576-577 (2003).

[7] W. Takashima, M. Fukui, M. Kaneko and K. Kaneto, *Jpn. J. Appl. Phys.*, **34**, 3786-3789 (1995).

[8] W. Takashima, M. Nakashima, S. S. Pandey and K. Kaneto, *Chem. Lett.*, in printing.

[9] W.-S. Huang, B. D. Humphrey, A. G. MacDiarmid, *J. Chem. Soc., Faraday Trans. 1*, **82**, 2385-2400 (1986).

[10] W. Takashima, S. S. Pandey and K. Kaneto, *Thin Solid Films*, **438**, 339-345 (2003).

[11] J.-C. Chiang and A. G. MacDiarmid, *Synth. Met.*, **13**, 193-205 (1986).

[12] H. Reiss, *J. Phys. Chem.*, **92** 3657-3662 (1988).

[13] P. Chartier, B. Mattes and H. Reiss, *J. Phys. Chem.*, **96**, 3556-3560 (1992).

[14] S. Ghosh and V. Kalpagam, *Solid State Ionics*, **60**, 149-152 (1993).

(Received October 10, 2003; Accepted November 15, 2003)