
原 著

Electro-synthesis and Electrochromism of Conducting Polymer Polypyrrole in Volcanic Spring Water

YU INNAMI¹⁾ and HIROMASA GOTO^{1)*}

(Received Aug. 24, 2011, Accepted Aug. 31, 2012)

天然火山性水における導電性高分子ポリピロールの 電解合成とエレクトロクロミズム

印南 雄¹⁾, 後藤博正^{1)*}

要 旨

火山性天然水を電解液として用い、導電性高分子ポリピロールの電解合成を行った。得られたポリマーの紫外可視吸収スペクトル、電子スピン共鳴、電気導度を測定し、これらの測定結果から高分子鎖に電気伝導を行うキャリアが発生していることが分かった。火山性天然水中に含まれるアニオン種が重合時に電解質として機能するとともに、重合後のポリマーのドーパントとなり、電気伝導に寄与したと思われる。

キーワード：温泉水、電気化学、紫外可視吸収スペクトル、電子スピン共鳴

Abstract

Electrochemical synthesis of polypyrrole in natural volcanic water was carried out. Ultraviolet-visible (UV-vis) absorption spectroscopy, electron spin resonance (ESR), and electrical conductivity measurement for the polymer were performed, and the results confirm generation of charge carrier in the polymer. Anionic species in the volcanic water play a role of electrolyte for the electropolymerization, and the anions as dopants contribute electrical conduction of the polymer.

Key words : Electrochemistry, Electron spin resonance (ESR), Hot spring water, Ultraviolet-visible (UV-vis) absorption spectroscopy

¹⁾Division of Materials Science, Faculty of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8573, Japan. ¹⁾筑波大学数理物質系 〒305-8573 つくば市天王台1-1-1. *Corresponding author : E-mail gotoh@ims.tsukuba.ac.jp, FAX 029-853-5128.

1. Introduction

Volcanic hot spring water (VW) has been familiar to people in the world (Deetjen, 1988). The composition of VW depends on the district. VW generally contains anions such as SO_4^{2-} and Cl^- . The anions in the VW can function as electrolyte. Especially, sulfate ions play a role of dopants of conducting polymers (Chiu *et al.*, 2005 ; Licona-Sánchez *et al.*, 2011). Therefore, the VW is applicable for electrochemistry. The VW also contains metal cations such as Fe^{2+} , Fe^{3+} and/or Zn^{2+} . These metal cations might aid polymerization reactions as catalysts.

Conducting polymers have been synthesized with 1) chemical method by using catalysts or oxidizers (Hino *et al.*, 2006 ; Phang and Kuramoto, 2009 ; Cao *et al.*, 1992) and 2) electrochemical method. Especially, synthetic procedure of electrochemical polymerization is quite simple. As shown in Fig. 1, the electrochemical polymerization is generally carried out by application of voltage between two electrodes in the electrolyte solution containing monomer. The resultant polymer is generally obtained on the anode (positive electrode) as thin films. Additionally, reference electrode is employed in the polymerization cell to monitor the voltage.

In the previous study, we synthesized polyaniline in the VW by chemical oxidative polymerization (Goto, 2010). In this research, we tried to obtain conducting polymer polypyrrole (Hara *et al.*, 2003 ; Matsubara *et al.*, 2004 ; Lu *et al.*, 2006) by using VW with electrochemical method, and examined its properties. The polymer thus obtained showed electrochromism (color of the polymer is tunable by applying voltage in the VW (Goto, 2007) and electrical conductivity. These results imply a possibility of application of VW for electrolytes, and the resultant electroactive polymer may be used as an ion sensor for VW.

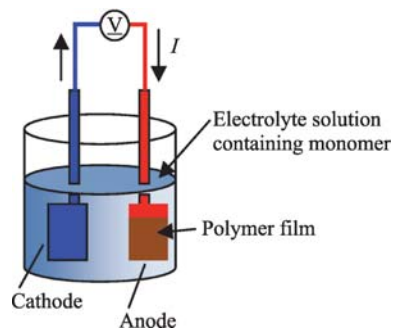


Fig. 1 Fundamental scheme of electrochemical polymerization.

2. Experimental

2.1 Materials

Pyrrole as a monomer was purchased from Tokyo Chemical Industry (TCI) Co., Ltd. and used without further purification. The transparent indium tin oxide (ITO) coated glass ($9\Omega/\text{cm}^2$) was employed for anode in the polymerization. VW from Owakudani hot spring in Kanagawa Prefecture was employed in this research. The sample water was obtained on Feb. 16, 2009. The VW was purified before using by filtration with a qualitative filter paper. Multi-channel type induced plasma coupling (ICP) analysis was carried out at the Chemical Analysis Division of Research Facility Center for Science and Technology of University of Tsukuba. The ICP analysis revealed that the VW contains Li, Be, B, Na, Mg, Al, Si, S, Ca, Mn, Fe, Zn, Sr and Ba.

2.2 Technique

Fourier transform infrared spectra (FT-IR) of the polymer were taken with a Jasco FT-IR 300 spectrometer by the KBr method. Ultraviolet-visible (UV-Vis) absorption spectroscopy meas-

urements were carried out at room temperature by using a Hitachi U-2000 spectrometer with a quartz cell. Electrochemical polymerization was carried out in VW using Eco chemie μ Autolab type III. The three electrode system consists of an ITO glass working electrode, a calomel electrode as a reference electrode, and a platinum wire as a counter electrode. Electron spin resonance (ESR) measurement of the polymer in solid state was carried out with a Jeol JES TE-200 spectrometer. The electrical conductivity of the polymer was measured at room temperature using Mitsubishi Lowrester-GP MCTP-T610 with MCP-TP06P probe by the DC four-point probe method.

2.3 Polymerization

Polymerization of pyrrole in water medium has been carried out by using surfactant (Amaike and Yamamoto, 2006), and template polymerization was conducted (McCullough *et al.*, 2009). In this study, electro-polymerization is carried out in the VW without use of surfactant.

The electrochemical polymerization was performed in the VW solution of 0.1 M pyrrole by repeated potential cycling at a scan rate of 10 mV/s with saturated calomel electrode (SCE) as a reference electrode at room temperature (25 °C). After three repeating scan, thick dark brown film appeared on the ITO glass. Pyrrole is not highly reactive in β position. However, crosslinking is partly considerable. Thus, polypyrrole has a straight-chain structure mainly (Fig. 2). The polymer thus obtained is abbreviated as PPy_(VW).

The PPy_(VW) film was insoluble in organic solvents. Thus, the molecular weight of the PPy(VW) couldn't be measured, it might be estimated to be <10000 (M_n).

3. Results and Discussion

3.1 FT-IR absorption spectroscopy

Figure 3 shows an FT-IR absorption spectrum of PPy_(VW) scaled from the ITO substrate. The absorption band at 3411 cm^{-1} which corresponds to N-H stretching was observed in Fig. 3. The polymer also shows the absorption band of a framework vibration of a pyrrole unit at 1622 cm^{-1} . These results indicate that pyrrole was polymerized in the VW under acid condition. The absorption band associated with C-H bending vibration was also observed at 1140 cm^{-1} . This band would disappear if the polymer formed a network structure completely. Therefore, PPy_(VW) yielded mainly a straight-chain structure and partially a network structure.

3.2 UV-Vis absorption spectroscopy

Figure 4 shows UV-Vis absorption spectra of PPy_(VW) film. The electro spectroscopic measurements were carried out in the monomer-free VW solution for the PPy_(VW) on ITO glass

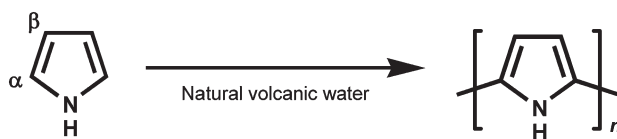


Fig. 2 Polymerization of pyrrole in VW.

working electrode. The electrochemical cell contains the working electrode, an SCE reference electrode, and a platinum wire counter electrode. The potential was switched from -0.25 V to 0.75 V and 0.75 V to -0.25 V (vs. SCE). In Fig. 4 (a), the doping band around 750 nm increases in an oxidative process. On the other hand, the doping band decreases in a reduction process (Fig. 4 (b)). These doping and dedoping processes were attributed to the dopants such as SO_4^{2-}

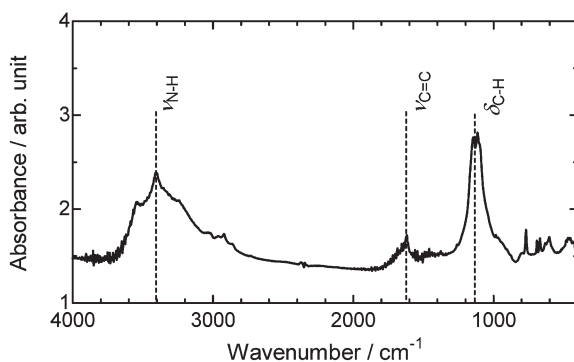


Fig. 3 FT-IR absorption spectrum of $\text{PPy}_{(\text{vw})}$.

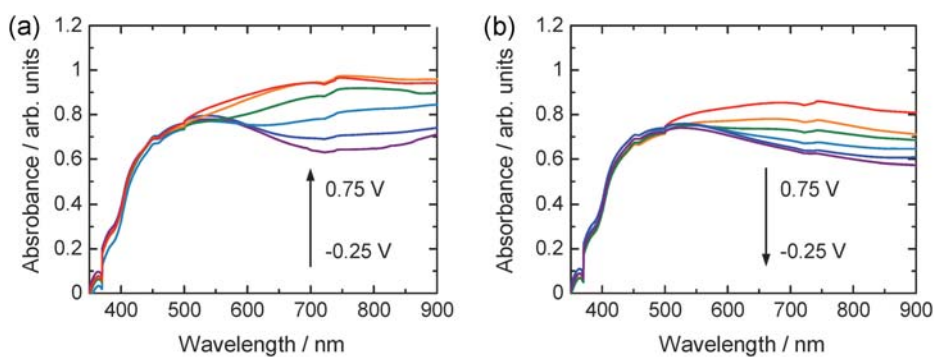


Fig. 4 UV-Vis spectra of $\text{PPy}_{(\text{vw})}$ film on ITO glass at the potential (a) from -0.25 V to 0.75 V (oxidation process), and (b) from 0.75 V to -0.25 V (vs. SCE) (reduction process).

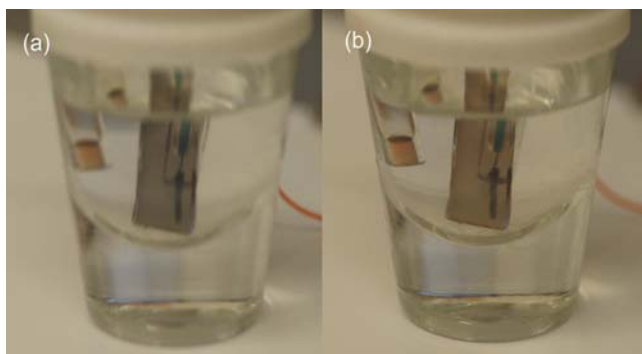


Fig. 5 $\text{PPy}_{(\text{vw})}$ film images at the potential of 0.75 V (a) and -0.25 V (b) (vs SCE).

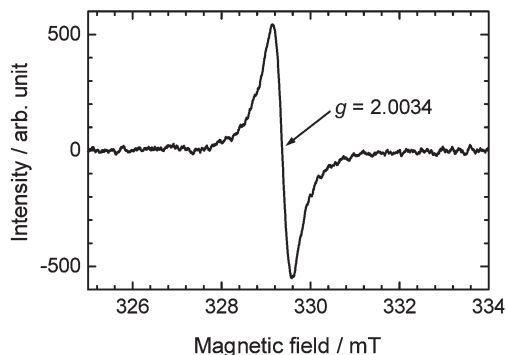


Fig. 6 ESR spectrum of PPy_(VW) at room temperature.

and HSO₄⁻ in the VW. Figure 5 shows the film images in oxidized state and reduced state. The polymer changes in color by applied voltage (oxidized form, 0.75 V, black ; reduced form, -0.25 V, brown), indicating change in electronic state of the polymer in the VW is observable by visible inspection. Therefore, the VW can be useful as electrolyte solution for electroactive polymers. Further study might enable to detect ions in VW with redox process of the electroactive polymers.

3.3 ESR spectroscopy and electrical conductivity

ESR spectroscopy of PPy_(VW) was measured at room temperature. Figure 6 shows ESR spectrum of PPy_(VW). The spectrum displays a symmetrical shape with $g=2.0034$. This signal is due to a presence of charge carrier such as polarons (radical cations in the polymer) along the polymer chain. The electrical conductivity of the PPy_(VW) film was to be 1.3×10^{-1} S/cm, implying the PPy_(VW) film shows moderate electrical conductivity as a conducting polymer.

4. Conclusion

Polypyrrole was electrochemically synthesized in the VW. The polymer thus obtained shows electrochromism. The redox state of the polymer in the VW can be detected through not only color but also change in potential during electrochemical measurements. This result might open for possibilities toward application of natural resources in electrochemistry. This study is a new trial for synthesis of polymers in the VW, and an unprecedented attempt in the fields of materials science. Our future subject is synthesis of natural polymers in VW. In this step, synthesis of conjugated polymer in VW was successfully carried out.

Acknowledgments

The author thanks Hakone Hot Spring Spa Supply Co. Ltd. (Kanagawa Prefecture, Japan) for generously providing the hot spring water sample. The author is grateful to the Engineering Workshop of University of Tsukuba for glasswork and the Analysis Center for the ICP measurements.

References

- Amai, M. and Yamamoto, H. (2006) : Preparation of polypyrrole by emulsion polymerization using hydroxypropyl cellulose. *Polymer Journal*, **38**, 703-709.
- Cao, Y., Smith, P. and Heeger, A. J. (1992) : Counter-ion induced processibility of conducting polyaniline and of conducting polyblends of polyaniline in bulk polymers. *Synth. Met.*, **48**, 91-97.
- Chiu, W., Travaš-Sejdić, J. Cooney, R. and Bowmaker, G. (2005) : Spectroscopic and conductivity studies of doping in chemically synthesized poly (3,4-ethylenedioxythiophene). *Synth. Met.*, **155**, 80-88.
- Deetjen, P. (1987) : Scientific fundamental data of Gastein, Forschungsinstitut Gastein-Tauernregion, Ausgabe in japanischer Sprache, Sem. Repots Salzburg-Austria, Auflage, **88**, 1-16, ISSN 0256-4173.
- Goto, H. (2007) : Optically active electrochromism in polyanilines. *J. Polym. Sci. Part A : Polym. Chem.*, **45**, 2085-2090.
- Goto, H. (2010) : Synthesis of polyaniline in volcanic hot spring water. *J. Hot. Spring. Sci.*, **60**, 134-144.
- Hara, S., Zama, T., Sewa, S., Takashima, W. and Kaneto, K. (2003) : Highly stretchable and powerful polypyrrole linear actuators. *Chem. Lett.*, **32**, 576-577.
- Hino, T., Namiki, T. and Kuramoto, N. (2006) : Synthesis and characterization of novel conducting composites of polyaniline prepared in the presence of sodium dodecylsulfonate. *Synth. Met.*, **156**, 1327-1332.
- Licona-Sánchez, T., Álvarez-Romero, G., Palomar-Pardavé, M., Galán-Vidal, C., Páez-Hernández, M., Ramírez Silva, M. and Romero-Romo, M. (2011) : Influence of the Cation Nature of the Sulphate Salt on the Electrochemical Synthesis of Sulfate-Doped Polypyrrole. *Int. J. Electrochem. Sci.*, **6**, 1537-1549.
- Lu, G., Li, C. and Shi, G. (2006) : Polypyrrole micro- and nanowires synthesized by electrochemical polymerization of pyrrole in the aqueous solutions of pyrenesulfonic acid. *Polymer*, **47**, 1778-1784.
- Matsubara, I., Hosono, K., Murayama, N., Shin, W. and Izu, N. (2004) : Synthesis and gas sensing properties of polypyrrole/MoO₃-layered nanohybrids. *Bull. Chem. Soc. Jpn.*, **77**, 1231-1237.
- McCullough, L. A., Dufour, B. and Matyjaszewski, K. (2009) : Polyaniline and polypyrrole templated on self-assembled acidic block copolymers. *Macromolecules*, **42**, 8129-8137.
- Phang, S.W. and Kuramoto, N. (2009) : Morphology studies of doped polyaniline micro/nanocomposites containing TiO₂ nanoparticles and Fe₃O₄ microparticles. *Polymer Composites*, **30**, 970-975.