Preparation of Conducting Polymers by Electrochemical Methods and Demonstration of a Polymer Battery

submitted by: Hiromasa Goto,* Hiroyuki Yoneyama, Fumihiro Togashi, Reina Ohta, Akitsu Tsujimoto, Eiji Kita, and Ken-ichi Ohshima
College of Engineering Sciences, Graduate School of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8573, Japan; *gotoh@ims.tsukuba.ac.jp

checked by: Daniel Rosenberg
Science Center, Harvard University, Cambridge, MA 12138

In 2000, Alan G. MacDiarmid, Alan J. Heeger, and Hideki Shirakawa received the Nobel Prize in chemistry for the discovery and development of conducting polymers (1–3). Previous to that discovery, all plastics were regarded as good insulators. The discovery of conducting polymers thus provides new avenues of research in both academic and industrial fields. The development of conducting polymers for practical applications has been rapid, and the range of new technologies includes solar cells, high-performance capacitors, field-effective transistors, organic electroluminescence devices, and electrochromic devices, representing a new approach of “plastic electronics” (4).

In the neutral state, conducting polymer precursors are inherently insulators. However, doping by the addition of low densities of an electron donor or acceptor yields a significant increase in conductivity. For example, a metallic-colored polyacetylene film prepared by the Shirakawa method (5) exhibits a greater than one-billion-fold increase in conductivity upon vapor doping with iodine. This effect, referred to as the insulator–metallic transition (6), derives from a change in the electronic state of polyacetylene by doping with an electron acceptor (or donor). The bandgap of polyacetylene before chemical doping is in the range of semiconductor–insulator with low carrier mobility. After doping, a mid-gap appears in the band structure, and carrier mobility increases. The mid-gap is referred to as the soliton level. The soliton in polyacetylene has been numerically simulated using the SSH model (7). Polarons (radical cations) and bipolarons (dication) are proposed as carriers in the electrical conduction of aromatic-type conducting polymers such as polyphenylene, polythiophene, polyaniline, and polypyrrole. The electrical conduction mechanism of conducting polymers differs from that of metals. Free electrons bear electrical conduction in metals, while solitons, polarons, and bipolarons function as carriers in conducting polymers. (Note also that the soliton, polaron, and bipolaron levels express energy levels in band structure of conducting polymers.) A photograph of a polyacetylene film is shown in Figure 1 as an example of such polymers.

In the many conducting polymer experiments reported to date, preparation has been performed by one of two methods: chemical polymerization using a catalyst, or electrochemical polymerization (8–12). Chemical polymerizations afford bulk polymers, usually in the form of a powder, that require further processing for practical applications, such as casting from an organic solvent. Hence, chemically prepared polymers are generally unsuitable for electrode reactions.

The product of the electrochemical polymerization is a film that adheres well to the electrode surface. Electrochemically prepared conducting polymers exhibit good electrochromic properties (electrochemically driven color change via a doping–dedoping mechanism). The electronic band diagrams of a conducting polymer are shown in Figure 2 (13). Electrochemical doping and dedoping of ions for a conducting polymer is achieved by a redox process in an electrolyte containing a supporting salt, where electrochemical oxidation liberates an electron from the polymer and injects an ion, and the reduction process replaces the electron in the polymers and releases the ion. The doped state is thus a charged state, while the dedoped state can be considered “discharged.” The electrochemical doping–dedoping process gives rise to a change in the electronic band structure of the conducting polymer and is accompanied by a visible color change. The redox state of the electrochemical system can be controlled by appropriate adjustment of the direction of current flow, providing responsive control of the doping–dedoping process.

Many types of conducting polymers have been reported, and the range of properties is extensive. For example, polypyrrole has good film-forming properties and displays moderate conductivity (ca. 10 S/cm), while polyaniline exhibits useful redox properties. For demonstration purposes, the utilization of monomers with high polymerization activity is preferable with respect to safety and convenience. Polyaniline and polypyrrole are suitable in this regard as low-cost polymers that can be prepared quickly by electrochemical polymerization using a water-based electrolyte.

Figure 1. Photograph of a clear polyacetylene film.
In the Classroom

The present demonstrations of electrochromism can be performed using both polyaniline and polypyrrole. Polymer battery demonstrations can also be achieved using polyaniline. The electrical conductivity of organic polymers represents excellent educational material, and synthesis experiments coupled with an introduction to the applications of conjugated polymers can be expected to encourage interest in materials sciences. Experiments using conducting polymers have been conducted by our group for both high school students and university students as an introduction to chemistry.

The demonstrations may be displayed with a video camera in a large lecture hall or by one teaching assistant for a group of up to 5 students (14). Although instructors perform the majority of the demonstration, students can participate by performing simple operations such as turning the power on and off under supervision. Individual students may prepare the electrolyte containing the monomer under the guidance of a supervisor. The dry-cell switchable power source and mini-motor with propeller used in the experiments were assembled prior to demonstration.

These demonstrations are designed with the aim of providing a snapshot of plastic electronics in an attempt to promote interest in the science of conducting polymers and electrochemistry and may be incorporated into the curriculum in electrochemistry or general chemistry. When students ask why the polymers change in color, the electrical conduction mechanism of conducting polymers can be explained using the chemical structure and the band diagram of the polymer. The doped and dedoped states in the band structure determine the wavelengths of optical absorption, which differ according to the state of the polymer. This is in effect a redox-induced transition. The doped state, having polaronic and bipolaronic components, allows electrical conduction.

Demonstration 1: Electrochromism

Two electrolytes containing a monomer (aniline or pyrrole) are prepared. The first electrolyte contains aniline (1 g) and sulfuric acid (1 mL) in 20 mL of water, and the pyrrole electrolyte contains pyrrole (0.3 g) and sodium chloride (table salt is sufficient, 1 g) in 20 mL water. The solution is stirred vigorously using a magnetic stirrer to induce the formation of a monomer salt, which is soluble in water. In the preparation of the aniline electrolyte, care should be taken to add sulfuric acid after the addition of aniline owing to the heat generated upon addition of sulfuric acid.

The monomer solution is then transferred into a 50 mL beaker. An indium tin oxide (ITO) glass and iron wire (paper clip) are connected to the anode and cathode via alligator clips (Figure 3). A potential of 3 V (2 × 1.5 V dry-cell batteries) is applied. In the aniline electrolyte, a deep blue thin film is deposited on the ITO anode within 1 minute. A black film is formed in the same manner from the pyrrole solution. The color changes are observable as the polymer film is deposited. The color of the solution sometimes changes as the film is prepared. This is because small molecular mass fractions of the polymer during the electrochemical synthesis may not adhere well to the glass surface. Application of lower voltage (e.g., 1.5 V or less) and longer polymerization time can minimize this effect.

A 20 mass percent sodium chloride in water solution is then prepared and transferred to a 12 cm Petri dish. An iron wire (paper clip) and the ITO slide covered with the polymer film are partially submerged in the saline solution, and alligator clips are connected to the ITO and the iron wire electrodes. Voltage is applied. A schematic of the experimental setup is shown in Figure 4. The color of the polymer changes as the polarity of the...
voltage is reversed, reflecting a change in the electronic state of the polymer. When polarity is reversed, delamination of the polymer from the glass surface sometimes occurs. This occurs because the high voltage injects large quantity of dopant (Cl\(^-\)) into the polymer rapidly, making it fragile. Low applied voltage (e.g., 1.5 V or less) or moderate electrode spacing can minimize this effect. Decreasing the distance between the anode and cathode leads to a lower IR (current–resistance) drop, allowing a decrease in the voltage applied to the polymer electrode. Polyaniline can exist in several different oxidation states (15, 16). Polaron and bipolaron may both exist in these polymers in the electrochemically doped state (oxidized state).

**Demonstration 2: Conduction Test**

The ITO glass covered with the polypyrrole film is gently dabbed with tissue paper to remove the electrolyte, and the surface is dried under an ambient atmosphere. Transparent tape is then applied to the polymer surface and peeled off, leaving the polymer adhering to the transparent tape. Doping of the film in the electrolyte during polymerization induces electrical conductivity in the film. A conduction test of the film can be performed using a multimeter or light-emitting diode (LED) connected to a 3 V power supply. LED emission in the conduction test indicates good electrical conduction by the polypyrrole film. The electrical conductivity of polyaniline is relatively low and does not produce a strong emission.

**Demonstration 3: Polymer Battery**

Conducting polymers can also be employed as charge storage materials for rechargeable batteries. Electropolymerized polyaniline deposited on the ITO glass or a stainless-steel plate, which is the anode in the electrolyte, functions as a rechargeable battery. This charge–discharge behavior can be demonstrated using the electrochemically polymerized aniline electrode coupled to a motor-driven propeller. A stainless steel anode is preferable for this demonstration because the size of film required is relatively large and stainless steel is much lower in cost compared to ITO glass. However, the use of ITO glass as an electrode allows the color change of the polymer to be readily observed during the charge–discharge procedure.

The polyaniline film is electrochemically deposited on a stainless-steel plate (5 × 10 cm) following the same procedure used in demonstration 1. In this case ca. 200 mL of electrolyte containing the aniline monomer is required, and a stainless-steel counter electrode of similar size is used instead of an iron wire. A piece of plastic window screen (5 × 10 cm) is used to separate the electrodes. The polymerization time in this case is longer than 1 minute to prepare a thick polyaniline film on the stainless-steel plate (Figure 5 top). The battery clips are disconnected after polymerization, and the alligator clips linked to the motor and propeller are connected to the two plates. The propeller initially rotates rapidly (Figure 5 bottom), and as the polymer battery discharges, the color of the polyaniline changes due to dedoping. After the motion has stopped, indicating that the charge has been exhausted, a voltage is applied to the polymer film by dry-cell batteries to restore the charged state. The recharge operation causes further electrochemical polymerization. Repeatable charge–discharge demonstrations are possible using this procedure.
The polymerization and doping processes are summarized in Scheme I. As the electronic structure of polyaniline is relatively complicated (17), the electronic state of polyaniline is denoted simply as either doped (oxidized) or dedoped (reduced), equivalent to the charged and discharged states, respectively. Electrochemical polymerization affords a polymer in the doped state and thus stores charge. This demonstration confirms that the electrochemical doping–dedoping (oxidization–reduction, charge–discharge) process changes the electronic state of the conducting polymer, which can be observed via color changes.

**Hazards**

Aniline is toxic by inhalation of the vapor, absorption through the skin, or swallowing. Preparation of aniline-based electrolyte should be conducted in a fume hood. Pyrrole is harmful by inhalation, ingestion, or skin absorption. Ingestion may be fatal. Long-term exposure may cause liver damage. Sulfuric acid is corrosive and must be added carefully to avoid excessive heating.

**Conclusion**

This demonstration of electrochromism, conduction testing, and polymer battery may provide visual impact and promote student interest in polymer chemistry and plastic electronics.

**Acknowledgments**

The authors are indebted to Hideki Shirakawa of University of Tsukuba and to Ayako Miyajima and Masako Hidaka of the National Museum of Engineering and Innovation Japan.

**Literature Cited**


**Supporting JCE Online Material**


Abstract and keywords

Full text (PDF)

Links to cited JCE articles

Color figures

Supplement

List of materials and equipment

A video of the polyaniline battery connected to the motor and propeller

Figure of the electronic structure of conducting polymers