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Corrosion Protection of Copper by Conductive Polypyrrole Films Incorporated with Inhibitors

インヒビターを含有した導電性ポリピロール膜による銅の防食

Dissertation to Attain the Academic Degree
Doctor of Engineering

By
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March 2014
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Chapter I

Introduction

1.1 Background of corrosion

Corrosion is one of the processes that are daily observed. Its aspects are commonly recognized in everyday life. The corrosion is the result of a thermodynamically driven process of a metal converting to a more stable state. On the earth this stable state is usually metal oxides that exist in the earth as ores from which the metal was refined.

The corrosion process significantly consumes social infrastructures and industrial plants. It was reported that the total cost of corrosion damage in the United States for the years 1999-2001 was about $276 billion. This was approximately 3% of the Gross National Product in the period [1]. What is worse is that corrosion of metallic structure possibly lead to human’s injuries and death. For example, on December 15, 1976 the collapse of the” Silver Bridge” over the Ohio River linking Point Pleasant carried 46 people to their deaths. The collapse was assumed to be caused by combination of mechanical stress and chemical corrosion [2].

Since the corrosion process is not stopped from the thermodynamics aspect, anti-corrosion strategy is focused on controlling the dynamics, i.e., slowing the kinetics, altering the mechanism of the process [3].

When one considers electrochemistry of the corrosion, the corrosion involves one or several oxidation reactions and one or several reduction reactions. These reactions occur at the metal surface and a couple of oxidation and reduction reactions form a
local corrosion cell. When one controls the process to reduce the rate of either or both of these processes, the rate of the overall corrosion process may be reduced.

A variety of techniques have been developed to control the dynamics of corrosion. The cathodic protection using either a sacrificial anode or an external power supply shifted the potential of the corrosive metal to the negative direction, slowing its rate of corrosion. Conversely, the anodic protection shifts the potential to the positive direction, maintaining a protective passive (oxide) layer on the metal surface and reducing the corrosion rate. The corrosion inhibitors usually consisting of small organic molecules adsorb on the metal surface and impede either oxidation of the metal or the reduction reaction.

At the present time, one of the most common corrosion controls involves application of organic coating to the metal. An active corrosion cell requires the presence of an oxidant at the metal surface as well as ion movement between the anodic and cathodic sites of the corrosion cell. Such ion movement in the case of atmospheric corrosion occurs within a thin layer of electrolyte that forms on the metal surface. The organic coatings reduce the rate of corrosion by decreasing the rate to access the oxidants (e.g., oxygen gas, water and ions) to the metal surface. The coatings also provide large resistance against ion movement at the interface (i.e., large ohmic polarization of the corrosion cell) which also contributes to reduction in the corrosion rate. For prolonged exposure period, water, oxygen gas and ions from the environment gradually penetrate the coating and reach the metal surface. Generally speaking, polymer coating unavoidably possesses nano- and/ or microscopic defects.
The defects promote the corrosion process. In any case, sooner or later corrosion starts at the defects and causes delamination of the coating which is induced by electrochemical corrosion reaction, especially, the delamination is promoted by cathodic reaction [4].

In order to restrain corrosive attack, pigments inhibiting corrosion are added to the paint and organic coating covering the metal surfaces. But nearly all powerful inhibitors may have detrimental effects on environment, when released in substantial amounts. One of the most efficient pigments is those containing chromates in which strontium chromate has been usually used. Because of their toxic and carcinogenic nature, however, their use has to be progressively decreased [5,6]. Hence, novel approaches are desperately sought for.

One of several new approaches studied as replacement of chromates is coating of intrinsically conducting polymer (ICP). The ICP coating for the corrosion inhibition was first reported for stainless steel in 1985 by DeBerry who opened a new door to protect metal against corrosion [7]. The stainless steel was passivated in sulfuric acid solution by oxidative property of the ICP. Since then, many corrosion researchers have been interested in the corrosion protection using ICP and presented a great number of papers.

1.2 Intrinsically Conducting polymer (ICP)

Most common polymers are non-conductive. They are used not only for structural purposes, but also for electrical isolation. In order to provide conductive property,
electrically conductive particles like carbon black and metal fibers are sometimes added to a polymer to form a conductive polymer blend. These blends are often called extrinsically conducting polymers and may be used in the field where electrostatic discharge (ESD) must be prevented, for instance, clean-rooms for IC production.

In contrast, the intrinsically conducting polymers (ICPs) described in this thesis possess electronic conduction abilities within their own molecular structure. The conductive behavior of the ICPs has a strong resemblance to semi-conductors and is likewise governed by charge carrier excess and depletion. A significant difference from inorganic semiconductors is the lack of long-distance three-dimensional ordering.

1.2.1 Historical background of ICP

Conductance in organic polymer substances has been known since more than a hundred years. In 1862, Letheby of the College of London Hospital produced a partly conductive material by anodic oxidation of aniline in sulfuric acid [8]. The material produced was probably a form of polyaniline. The material with the unique nature slipped into oblivion for several decades. In 1916, Angeli reported on the chemical polymerization of pyrrole [9], which was known to form a conductive pyrrole (PPy) black under influence of ambient oxygen. Conductivity in polymers was also reported by Hatano et al. in 1961 [10]. The polyacetylene had a conductance of $10^{-5}$ S/cm, and had been thought to consist of isolators, at that time. Electropolymerization of pyrrole was first reported by dall’Ollio in 1968 [11].
In 1977, American scientists MacDiarmid and Heeger and their Japanese colleague Shirakawa obtained the polyacetylene with a high conductivity and metal-like properties [12, 13]. The conductance of polyacetylene was observed to increase from a semi-conductor to metallic range with a conductivity of up to $10^5 \text{ S/cm}$ after partial oxidation of the polymer by exposure to halogen vapors (Fig. 1-1). This discovery became basics on which wide range of application was achieved, and the discovery brought them the Nobel Prize in the year 2000 [8].

Since the discovery of polyacetylene there has been much research on ICPs and many new ICPs have been synthesized. The most important and practical ICPs are polypyrrole (PPy), polythiophene (PTh), polyaniline (PAni) and poly(3,4-ethylenedioxythiophene) (PEDTO). All the polymers involve conjugated C-C chain in their molecular structure (Fig. 1-2) which is the basis for the conductive behavior.
Many potential applications have been suggested for the ICPs such as sensor [14], electrochromic device [15], corrosion inhibitor [16,17], and electrochemical actuator [18]. Many of these applications are relatively new and further improvement can be expected in the near future.

### 1.2.2 Conducting mechanism

ICP shares several characteristics, including macromolecular character and electrical transport properties. The common structure in ICP is an altering single and double bond, i.e., conjugated bond, along the polymer backbone. As in the case with polyacetylene, which processed the simplest conducting polymer structure, the electrical transport characteristics are obtained by exchange of single and double bond on the backbone for the polymer (Fig. 1-3(a)). The subsequent electrical conductivity is often mistakenly visualized from resonance structures and the mobility of electrons
as depicted for polyacetylene in the Figure. In fact, conjugation alone, however, is not sufficient for conductivity. To make polymer more conductive the positively charged site-radical pairs have to be introduced into polymer backbone. The formation of the positively charged site-radical pair (radical-cation) can be induced by oxidation of the conjugated structure in C-C chain. The positive charged site in the polymer C-C chain requires insertion of negatively charged particles from the outer environment to maintain the neutrality. When the ICP exists in the solution, doping of anions occurs from the electrolyte to the CP. The subsequent electrical conductivity is provided by addition of irregularity in the conjugated structures and the movement of a pair a positively charged site and an electronic radical is depicted for polyacetylene in Fig. 1-3(b).

\[ \text{(a)} \]
\[ \text{(b)} \]

**Fig. 1-3** (a) Resonance of electronic states in the conjugated C-C chain in polyacetylene. (b) Conductive polyacetylene in which a pair of a positively charged site and a radical is inserted in the conjugated structure and the movement of the pair.

1.2.3 Synthesis of ICP
The polymerization of an ICP is performed in the solution containing the individual monomer by either chemical or electrochemical process. In chemical polymerization, an oxidant is consumed to polymerize the monomer and anions are doped as a counter part of the oxidative CP, as shown for the polymerization of pyrrole in Fig. 1-4.

This chemical approach to producing ICPs is widely used in industry. The chemically oxidizing polymerization often results in the formation of a conducting polymer powder, which generally exhibits the lower conductivity than the electrochemically prepared conducting polymer.

Electropolymerization for synthesis of ICPs is preferred to chemical polymerization because it effectively controls the polymerization process and the amount of the polymer on the surface of metal substrate. Most of ICPs can be electrochemically produced by anodic oxidation. There have been many reports concerning electropolymerization process of PPy on metals like iron, carbon steel or stainless steel.

During the oxidizing electropolymerization of Py, two reactions take place on electrode: i) oxidation of Py monomer, and ii) oxidation of polymer backbone.
producing positive charges. The positive charges are compensated by the anions doped from electrolyte. This reaction is identified as a doping process. Fig. 1-5 shows the electropolymerization reaction of pyrrole (1) in which polymer film is formed through radical polymerization and deposited on electrode surface. Reaction (2) represents simultaneous removal of electron and doping of counter anions.

\[
\begin{align*}
\text{(1)} & \\
\text{(2)}
\end{align*}
\]

Fig. 1-5 The mechanism of the Polypyrrole polymerization

PPy can be obtained on substrate surface by potentiodynamic, potentiostatic, and galvanostatic polymerization, or modifications of those methods.

The advantages of electrochemically synthesize methods are including: 1) no oxidizing agents for preparation, 2) preparation of the polymer doped with different ions, 3) better adherence of the polymer on the substrate in comparison with chemically synthesized polymers, and 4) controlling the thickness and morphology of conductive polymers film.
1.3 Inhibition of Copper corrosion using ICPs

ICPs have been widely applied to corrosion protection. Environmentally friendly nature and high effectiveness on the corrosion protection, ICPs have been assumed to become one of candidates for proper replacement of conventional coatings to combat corrosion in different environments. Corrosion protection using ICP was first suggested by DeBerry [19] in 1985, who presented that the stainless steel covered by PAni was kept in the passive state for relatively long period in sulfuric acid solution. Wessling [20] then pointed out that the conducting polymer coating of PAni and PPy possibly possessed self-healing properties, in which the passive oxide between the substrate metal and the conducting polymer could be spontaneously reformed at a flawed site by oxidative capability of the conducting polymer. Since then, conductive polymers have been extensively applied to corrosion protection. A large number of papers have been published on synthesis of conducting polymer on Fe [21-24] and Al [16,25-27] substrates. Several authors have reviewed the use of conducting polymer for the corrosion protection of useful metallic materials [16,17,21].

According to the previous papers, several mechanisms of corrosion protection using conductive polymers have been proposed. One mechanism is the so-called “ennobling mechanism” or “anodic protection mechanism” that is based on the assumption that conductive redox polymers such as polyaniline or polypyrrole under the oxidized state act as an oxidizer, improving the passive oxide layer at the polymer/metal interface and maintaining the metal in the passive state [28]. The other
is the physical barrier mechanism. In the barrier mechanism, the polymer coatings work as a barrier against the penetration of oxidants and aggressive anions, protecting the substrate metals. This barrier effect is similar to paint coating which inhibits the substances from penetrating to the substrate steel [21]. In addition to the two mechanisms, some other mechanisms were also proposed. For example, ICPs shift the reaction site of oxygen reduction to the surface of ICPs and the delamination was inhibited, because the OH ions formed by the cathodic reaction at the polymer/ metal interface promotes much the delamination [29,30].

1.3.1 Application of ICPs to corrosion protection of copper and its alloys

Copper is widely used in many industries such as microelectronics for wiring, electromagnetic interference (EMI) shielding, electrostatic dissipation, etc. Despite the fact that copper is noble, it easily corrodes in a variety of environments. Particularly, it is more susceptible to the presence of chlorides and sulfur.

There have been only a few studies on the corrosion protection of copper by ICPs in spite of its use in a wide range of technological applications.

Brusic et al. [31] have investigated the use of PANi and its derivatives for the corrosion protection of copper with possible application to the microelectronics industry. Unsubstituted PANi in base form (undoped) and salt form (doped with either HCl or dodecylbenzenesulfonic acid) were investigated. Additionally, substituted PANi with either ethoxy or propyl groups in the ortho position were evaluated in either the base or salt form. The polymers were spin coated (95-510 nm thickness) onto Cu
foils or onto Cu-coated silicon wafers. The substituted PANi in the base form showed the best corrosion protection, even superior to benzotriazole (BTA) which was often used for the copper-corrosion inhibitor. The protection was performed by complete inhibition of the oxygen reduction reaction.

PPy is one of the most promising conducting polymers, because of its high conductivity, stability, processability, and ease of synthesis. Many researchers have presented the papers on the protection of corrosive metals by electrochemically prepared PPy.

Initial work exploring corrosion inhibition of copper alloys using PPy was performed by Breslin [32] in 2002. A PPy film was formed on Cu electrode from a near neutral oxalate solution. The growth of these films was facilitated by the initial oxidation of the copper electrode in the oxalate solution to generate a copper oxalate pseudo-passive layer. After that, in 2004, they reported a PPy film on copper electrodeposited from a dihydrogen phosphate solution [33], and recently they reported the PPy film electrosynthesised from a salicylate solution [34] for corrosion protection of copper in NaCl solution by means of cyclic voltammetry. The polymer coating formed was effective in protecting copper and was stable for periods exceeding 2 weeks of immersion in 0.6 M NaCl.

Chane-Ching et al. [35] studied the electrochemical synthesis of PPy film on copper from different electrolyte solutions. Oxalic acid, sodium oxalate, sodium/potassium tartrate and sodium salicylate were used as electrolytes and compared in terms of easiness for PPy deposition, and film characteristics.
Electrochemical measurements in these electrolytes with and without pyrrole demonstrate that copper can be efficiently passivated before polypyrrole electrodeposition. Moreover, FT-IR experiments revealed the chemical constitution of the thin passivated layer formed prior to the pyrrole electropolymerization and preventing copper corrosion without inhibiting the polymer formation.

Sharifirad et al. [36] studied the deposition of PPy film in citric acid, sodium acetate, and sodium benzoate solutions. All of them make it possible to prepare PPy on copper. The electrochemical conditions for PPy deposition as well as corrosion behaviors of the polymers were obviously different. It was shown that the corrosion protection of the PPy films formed highly depended on the solution for polymer formation, and sodium benzoate was the most favorable environment for the formation of PPy on copper surface.

Liesegang et al. [37] obtained smooth and flexible PPy films by electrochemical oxidation of pyrrole on an electropolished Cu electrode in an aqueous dodecylbenzene sulfonic acid (DBSA) medium. It was found that the electropolished copper surface was partially passivated by Cu$_2$O. The interfacial layer between the PPy/DBSA film and Cu substrate was also confirmed by time-of-flight secondary ion mass spectrometry (TOF-SIMS).

Tuken et al. [38] synthesized the PPy film on brass and copper electrodes from oxalic acid solution. The corrosion-protection performance of PPy coated samples was investigated in H$_2$SO$_4$ solution by the electrochemical impedance spectroscopy, anodic polarization curves and open circuit potential (E$_{ocp}$)-time curves. It was
shown that PPy coating could provide protection against the corrosion of copper and brass. The protective behavior was brought about by the barrier property of the coating against the attack of corrosive environment. After this paper, the authors [39] utilized a PPy/PTh bi-layer to protect the copper corrosion in NaCl solution. The PTh coating was achieved on the PPy coated copper electrode.

In addition to the PPy film for protection of copper alloy corrosion, other ICPs were also reported and the ICPs also exhibited corrosion resistance against the corrosion.

Redondo et al. [40] synthesized a poly(N-methylpyrrole) film on copper from an oxalic acid solution for corrosion protection. A potential higher than 2 V (SCE) was needed to generate the polymer, which resulted in the overoxidation state. The overoxidized polymer working as a physical barrier effectively inhibited the copper corrosion in NaCl solution.

Patil et al. [41] reported the synthesis of poly(o-toluidine) (POT) coating for corrosion protection of copper in chloride solution, and the results indicated that the POT as corrosion protective coating on Cu reduced the corrosion rate of Cu by 1/40. After this paper, the authors synthesized the poly(2,5-dimethylaniline) coatings on copper from salicylate solution [42]. The corrosion rate of copper in 3% NaCl solution was reduced by 1/31 due to the coating of poly(2,5-dimethylaniline).

Poly(o-ethyl aniline) (POEA) [43,44] coatings were synthesized on copper (Cu) by electrochemical polymerization of o-ethylaniline in salicylate solution. The performance of poly(o-ethylaniline) as protective coating against corrosion of Cu in
aqueous 3% NaCl was assessed by potentiodynamic polarization and EIS. The corrosion rate of POEA-coated Cu is found to be 70 times lower than that of uncoated Cu.

Duran et al. [45] obtained the poly(N-ethylaniline) (PNEA) coatings by cyclic voltammetry on copper in oxalic acid solution. Potentiodynamic polarization and EIS studies revealed that PNEA coatings protected copper against corrosion in aggressive sulfuric acid solution.

Bereket et al. [46] studied the Poly(pyrrole-co-N-methyl pyrrole) copolymer and poly(pyrrole)/poly(N-methyl pyrrole) bilayer composites for corrosion protection of copper in H2SO4 solution. It was found that copolymer and bilayer coatings were found to have the higher protection efficiency than that of single polypyrrole coating.

In addition of the above various conducting polymers, Poly(o-anisidin) P(OA) [47], and poly(m-phenylenediamine) [48] were also electrosynthesized for protection of copper against corrosion.

1.3.2 Issues in the application of ICPs for corrosion protection

When a researcher performs the electropolymerization of ICP on metal, there are some issues that they will be faced. One of the issues for the electrosynthesis of ICP is that the active dissolution of the metal prevents the polymer deposition. Although copper was classified as one of the noble metals, copper and its alloys were also suffered from the dissolution of the substrate during PPy deposition. A successful electro-polymerization process on oxidizable metals requires a careful choice of
media in which the metal should be passivated without hindering the polymerization process of the polymer. As previously reported, the PPy formation and its protection property highly depended on the electrolyte solution. In order to obtain durable and adhesive of PPy layers for the corrosion protection, thus, a selection of the proper solution is required.

When ICPs were deposited on metal, the galvanostatic methods may be preferred, because it allows to easily control the thickness of deposited ICP film by the charge passed. A typical curve of potential-charge or potential–time may be composed of an initial potential plateau and potential peak followed by the second potential plateau. Although the PPy deposition process has been discussed, the detail mechanism has not been understood. To clarify the detail, new experiment and new finding may be required.

The protection mechanism of the ICPs has still been under argument, although several protection mechanisms of the ICPs have been proposed.

A more complete overview over the research on conducting polymers for corrosion protection is given for non-ferrous and ferrous metals by Tallman et al. [16] and Spinks et al. [17]. It seems to be certain that coatings containing ICPs provide corrosion protection under some corrosion conditions, especially in the absence of defects. However, in the presence of relatively large defects, the polymers are often observed to fail to protect the substrate. Thus, introduction of the self-healing property of the polymer may be essential, when one considers the effective protection of metals by ICPs.
1.4 Purpose of this study

In this thesis, new protection coating of conducting polypyrrole (PPy) against the corrosion of copper is developed. For the development of the coating, we discuss the selection of solution for the PPy preparation and formation mechanism of the PPy coating by using various techniques of surface analysis. To survey the protection mechanism against copper corrosion in sodium chloride solution, we apply to it electrochemical techniques of usual polarization as well as electrochemical impedance spectroscopy (EIS) and electrochemical quartz crystal microbalance (EQCM).

From the results in this thesis we successfully prepared two effective coatings for the protection of copper against corrosion; PPy coating doped with phytic acid ions and PPy coating doped with oxalate ion and benzotriazole (BTA).

1.5 Construction of this thesis

The thesis is constructed by 6 chapters.

In Chapter 1, the background and history of the conducting polymer coating for the corrosion protection of metals, especially on copper and copper alloys are introduced. Further the purpose and structure of this thesis are described.

In Chapters 2, the PPy film formed in phytic acid solution on copper for corrosion
protection is discussed.

In Chapter 3, the pH dependence is discussed to prepare the PPy-IP$_6$ film for the corrosion protection of copper.

In Chapter 4, the protection mechanism of the PPy-IP$_6$ coating in aqueous sodium chloride solution is discussed by using electrochemical quartz crystal microbalance (EQCM) and electrochemical impedance spectroscopy (EIS).

In Chapter 5, the effect of the BTA on PPy formation on Copper and its corrosion protection is discussed.

In Chapter 6 the finding in this thesis was summarized.

1.6 References


Chapter II

Electrochemical synthesis of polypyrrole films on copper from phytic acid solution for corrosion protection

2.1 Introduction

Copper has excellent thermal conductivity, good corrosion resistance and mechanical workability. It is thus widely used in heating and cooling systems [1,2]. Severe corrosion of copper and its alloys, however, has been reported in various environments, especially in the presence of chloride ions [3-5]. To prevent or reduce the corrosion of copper, corrosion inhibitors [1,6-8] and sol-gel coatings [9-11] have been proposed. As corrosion inhibitors, azole, benzotriazole (BTA) and their derivatives have been widely investigated.

The application of conducting polymers to protect copper against corrosion has been reported by several authors [12-18]. One difficulty in the formation of conducting polypyrrole (PPy) on metal is active dissolution of the metal in a corrosive electrolyte, which inhibits the oxidative polymerisation of the pyrrole (Py) monomer. One approach to overcome this difficulty is the use of an electrolyte that includes an appropriate anion that deposits the complex compound with the dissolved copper and induces copper passivity. Electropolymerization of the monomer can then begin on the passivated copper. For the above reason, various acid solutions and the corresponding salts, such as oxalic acid [19], phosphoric acid [20], sodium salicylate [21], dodecylbenzene sulfonic acid (DBSA) [22], oxalate media [18], sodium tartrate
[23] and saccharate [16], have been studied for the electropolymerization and deposition of PPy on copper. For the corrosion protection, durable stability and adhesion of the PPy layer is required. For it, we assume that a solution containing an anion inhibitive against copper corrosion may be suitable to the electropolymerization medium of PPy. In this presentation, we select aqueous phytate (Phy) solution for the medium. The phytate anion has been reported to easily form a chelating compound with copper and to possess the inhibitor property of copper [24,25].

1, 2, 3, 4, 5, 6 Hexakis (di-hydrogen phosphate) myo-inositol (Fig. 2-1), known as phytic acid (IP₆), was first identified in 1855 [26]. Its salt (phytate) is widely present in nature (plant, animal, and soils), mainly as calcium, magnesium and potassium mixed salts. The salts protect seeds against oxidative damage during storage. Phytic acid and phytate are precipitated by reaction with polyvalent cations. Due to their attractive advantages, including low cost, availability, and nontoxicity, phytic acid and its salts have been widely used in many industrial areas, such as food, medicine, and painting [24,25,27,28]. The highly chelating potential of phytate also provides anticorrosive properties against metal corrosion [29,30]. It was reported that phytic acid and phytate could be used as primers for organic painting on metal [31].

![Figure 2-1: Structure of phytic acid (IP₆)](image)

Fig. 2-1 Structure of phytic acid (IP₆)
In this work, protective and stable PPy films were directly electrosynthetised on copper from aqueous phytate solution. Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM) were used to study the electrodeposition process. The corrosion test in 3.5% NaCl solution showed that the PPy layer doped with phytate (PPy-IP$_6$) allowed the copper to maintain the passive state for longer than 750 h.

2.2 Experimental

2.2.1 Materials and sample preparation

Pyrrole (Py) monomer purchased from Tokyo Chemical Industries (99 wt.% purity) was used without any pre-treatment. Phytic acid was purchased in the form of aqueous solution at 50 wt.% concentration from Wako Pure Chemical. All other reagents (analytical grade) were also obtained from Wako Pure Chemical. The solutions were prepared using double distilled and subsequently deionised Millipore water.

A copper sheet (99.99 wt.% pure and 2 mm thick) was cut into a rectangular sheet with dimensions of 25 mm × 15 mm. An exposure surface area of 10 mm × 10 mm of the rectangular copper was used for polymer deposition, and the other surface was covered with insulating silicon resin. Before each experiment, the exposed surfaces were sequentially polished with #220, 400, 600, 800 and 1000 SiC paper, degreased with acetone and ethanol, and finally washed with pure water.
2.2.2 Electropolymerization

Electropolymerization was performed under constant current control in a three-electrode electrochemical cell with a volume of approximately 50 cm³. The potential of the working electrode was measured with respect to Ag/AgCl/ sat. KCl (SSE) and the counter electrode was platinum foil. All the potential in this paper was plotted with respect to the Ag/AgCl/ sat. KCl (0.197 V vs. SHE).

The solution used for electropolymerization was 0.1 mol dm⁻³ (M) phytic acid containing 0.5 M Py monomer. The solution pH was adjusted to 6.0 by the addition of sodium hydroxide, because it was reported that copper could be effectively protected by phytic acid solution at pH 6 [25]. Prior to the electrochemical experiments, the solutions were deaerated by bubbling pure nitrogen for longer than 15 minutes.

2.2.3 Characterisations

The surface morphology of the PPy layer doped with phytate (PPy-IP₆) on copper was investigated using SEM (JEOL JSM-6510LA). The PPy-IP₆ layer was analysed with Raman spectroscopy (RS) and infrared reflection absorption spectroscopy (IR-RAS). For RS, a Raman spectrometer (Bunko-Keiki M30-TP-M) was used, in which the excitation was produced by a YVO₄ solid-state laser beam at 532.0 nm wavelength, and the detection of scattering light was achieved with a highly sensitive CCD (Andor DO4041A). The excitation laser power was controlled so that it was lower than 5 mW to avoid damaging the PPy films. IR-RAS spectra were measured by a JASCO FT-IR 4200 with a reflection apparatus (RAS PR041-H) in the
wavenumber range of 2500-600 cm\(^{-1}\) with a resolution of 4.0 cm\(^{-1}\). XPS measurements were performed with a JEOL-9200 with a Mg K\(\alpha\) X-ray source at 1253.6 eV. The binding energies were calibrated to the Au 4f\(_{7/2}\) electron peak at 84.00 eV. A Gaussian form was assumed in the deconvolution of the spectra, in which the full widths at half maximum (FWHM) were kept constant for all components in the spectrum. The element depth profile was measured by glow discharge optical emission spectroscopy (GD-OES) using a Horiba JY-5000RF spectrometer.

2.2.4 Corrosion test

Corrosion of the copper covered with PPy-IP\(_6\) was studied at 25 ± 1 °C under open air conditions in 3.5% NaCl solution, in which the open circuit potential (OCP) and electrochemical impedance spectroscopy (EIS) were measured. EIS spectra were measured at the OCP by a frequency response analyser (FRA; NF Circuit Design 5020) connected to a potentiostat that was specially designed in our laboratory. The measurement was performed in the frequency range from 20 kHz to 10 mHz with an AC voltage of 10 mV rms.

The amount of copper ions dissolved in the NaCl solution was measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES; Thermo-ICAP 6000).

2.3 Results

2.3.1 Electrochemical synthesis of PPy films on copper
Fig. 2-2 shows the potential change as a function of electric charge passed of the copper electrode during constant current polymerisation of PPy in phytic acid (IP₆) solution containing Py monomer. The potential initially increased from the immersion potential of –0.67 V to a peak and then gradually decreased to a plateau at which black PPy was observed on the copper surface. The initial potential increase may correspond to the nucleation of PPy. The charge passed to the peak potential was approximately 0.05 C cm⁻². The three-dimensional growth of PPy occurred in the subsequent potential plateau region. The potentials at the peak and in the plateau increased as the applied current density (CD) increased.

Fig. 2-2 Potential change with charge during electropolymerisation of PPy on copper at current densities of 1.0 (---), 2.0 (-----) and 5.0 mA cm⁻² (--------), in a pH 6 solution of 0.1 M phytic acid and 0.5 M Py monomer.

2.3.2 Characterisation of the PPy films

2.3.2.1 Surface morphology

The surface morphology of the PPy doped with phytate (PPy-IP₆) on copper was
observed by SEM. Examples of SEM micrographs are shown in Fig. 2-3, in which the PPy layer was formed by 2 C cm\(^{-2}\) charge at CD of 0.5 (Fig. 2-3(A1) and (A2)) and 5 mA cm\(^{-2}\) (Fig. 2-3(B1) and (B2)). In Fig. 2-3(A1) and 2-3(A2), the PPy-IP\(_6\) layers show a globular morphology with particle sizes ranging from 1 to 2 \(\mu\)m in diameter. Cauliflower morphology of polypyrrole was observed in Fig. 2-3(B1), in which PPy-IP\(_6\) layers were composed of compactly conglomerated PPy clusters with sizes in the range 5-10 \(\mu\)m. From the increased magnification in Fig. 2-3(B2), larger PPy clusters were observed than those in Fig. 2-3(A2); these clusters consisted of small spherical grains that were 0.5-1 \(\mu\)m in diameter.

The thickness was estimated from a cross-sectional view of the PPy-IP\(_6\) layer by SEM. The estimated thickness-to-charge ratio was approximately 2 \(\mu\)m C\(^{-1}\) cm\(^{-2}\).

**Fig. 2-3** SEM micrograph of PPy-IP\(_6\) films formed at (A) 0.5 mA cm\(^{-2}\) for 4000 s and (B) 5.0 mA cm\(^{-2}\) for 400 s.
2.3.2.2 Raman and IR spectra

The PPy-IP₆ layer on copper was examined by infrared reflection absorption spectroscopy (IR-RAS) and Raman spectroscopy (RS). For IR-RAS, the IR reflectance \( R \) from copper covered with the PPy-IP₆ layer was normalised to the reflectance \( R_0 \) of bare copper without a PPy film and converted to absorbance using the equation below.

\[
\text{Absorbance} = - \log\left(\frac{R}{R_0}\right) \quad (2-1)
\]

Fig. 2-4(A) shows the IR-RAS spectrum of PPy-IP₆ formed on copper. The absorption peak positions in the spectrum were in agreement with the previous reports on PPy [32-35]. The strong bands from 1670 to 1400 cm⁻¹ were assigned to the stretching mode of C–C=C conjugative backbone and C–C ring stretching mode, respectively [32]. The weak peaks at 1367 and 1248 cm⁻¹ were related to C–C stretching and C–N stretching of the Py ring, respectively [33,34]. The peak at 1042 cm⁻¹ responded to –N–H in-plane deformation. The peak at 932 cm⁻¹ was related to C–H out-of-plane deformation [34,35]. Fig. 2-4(B) shows the IR-RAS spectrum of a thin IP₆ layer. To measure the IR-RAS spectrum, 10 μL of phytic acid solution at pH 6 was dropped on stainless steel and immediately dried in vacuum. The thin layer of IP₆ thus formed on the stainless steel was measured by IR-RAS. Although there is a small difference in wave number compared to the reference data, the peak positions in the IR-RAS spectrum of IP₆ were in agreement with the previous reports [36-38]. The peaks at 910, 1153, 1031 and 1245 cm⁻¹ were assigned to the vibration of P–O–C (910 and 1153 cm⁻¹), P–OH and P=O, respectively [36-38]. The absorption at 1553 cm⁻¹
was assigned to the vibration of the C–C bond in the IP₆ molecule. By comparing the absorption peaks of the PPy-IP₆ layer with those of IP₆ in the C–C vibration region of 1550–1600 cm⁻¹, the shoulder at 1551 cm⁻¹ in Fig. 2-4(A) most likely originated from the C–C vibration of IP₆ doped in the positively charged PPy. The broad bands above 1200 cm⁻¹ in Fig. 2-4(A) were also assumed to be attributable to overlapping of the –P=O vibrations upon PPy ring deformation. The weak absorption at 863 cm⁻¹, assigned to P–O stretching in IP₆, was shifted by doping in PPy [38].

![Fig. 2-4 IR-RAS spectra of (A) a PPy-IP₆ layer on copper and (B) IP₆ on stainless steel. The PPy-IP₆ layer was formed in phytic acid solution at current density 1.0 mA cm⁻² for 2000 s.](image)

The PPy-IP₆ layer was examined by Raman spectroscopy. Fig. 2-5(A) and 2-5(B) show the Raman spectra of the PPy-IP₆ layer and the solution of phytic acid at pH 6, respectively. The Raman peaks of the PPy-IP₆ layer in Fig. 2-5(A) were assigned as follows: the peak at 1597 cm⁻¹ to the stretching of conjugative backbone C–C=C–, the peak at 1405 cm⁻¹ to N–C ring stretching, the peak at 1324 cm⁻¹ to C–C ring stretching and the peak at 1049 cm⁻¹ to –N–H in-plane bending [33,35]. The peaks at 990 cm⁻¹
and 940 cm\(^{-1}\) were due to the ring deformation [39] and –C–H out-of-plane deformation [40], respectively. In the Raman spectrum of IP\(_6\) in the solution at pH 6, shown in Fig. 2-5(B), five peaks at 506, 846, 1076, 1363 and 1636 cm\(^{-1}\) were observed. The peaks at 506 and 846 cm\(^{-1}\) were assigned to the –O–P–OH stretching, while the peaks at 1076 cm\(^{-1}\), 1363 cm\(^{-1}\) and 1636 cm\(^{-1}\) were assigned to –P=O deformation, C–H deformation and H\(_2\)O bending, respectively [41-43]. By comparing the two Raman spectra in Fig. 2-5, it was found that two weak peaks at 508 and 860 cm\(^{-1}\) of the PPy-IP\(_6\) layer responded to vibration of the –O–P–OH group and that the weak peak at 1079 cm\(^{-1}\) was most likely related to P–OH stretching in IP\(_6\). The peak at 1360 cm\(^{-1}\) could be assigned to C–H deformation in IP\(_6\).

**Fig. 2-5** Raman spectra of (A) the PPy-IP\(_6\) layer and (B) aqueous phytic acid solution at 0.1 M concentration. The PPy-IP\(_6\) layer was formed in phytic acid solution at current density 1.0 mA cm\(^{-2}\) for 2000 s.

### 2.3.3 Corrosion test in NaCl solution of copper covered with PPy

#### 2.3.3.1 Open circuit potential

The OCP of copper covered with the PPy-IP\(_6\) layer in 3.5% NaCl solution was
monitored as a function of immersion time. The result is given in Fig. 2-6, in which the OCP of bare copper is also plotted for comparison. The OCP of copper covered with PPy-IP₆ initially decreased and then increased to its maximum value at 150 h. The OCP stayed constant for approximately 200 h and then gradually decreased to ~0.05 V at 750 h. For bare copper, the OCP dropped to ~0.2 V in the initial 3 hours and then remained constant during the immersion for 800 h. On the copper covered with PPy-IP₆, no corrosion products were observed in the entire immersion time of 800 h, although green-coloured corrosion products appeared on the bare copper immediately after the immersion began.

![Graph showing OCP vs. Time](image)

**Fig. 2-6** Open circuit potential (OCP) in 3.5% NaCl solution of (A) bare copper and (B) copper covered by PPy-IP₆ film. The PPy-IP₆ layer was formed in phytic acid solution at constant current density 5.0 mA cm⁻² for 400 s.

2.3.3.2 Amount of Cu ions dissolved during immersion

Fig. 2-7 shows the amount of copper ions dissolved from bare copper and copper covered with PPy-IP₆ during immersion in 3.5% NaCl solution. In Fig. 2-7, the amount was calculated from the concentration for the unit surface area of the copper.
For copper covered with PPy-IP₆, little Cu ions dissolved in the initial 24 h immersion. The amount of copper ions gradually increased with the immersion time; however, it remained relatively low. The average dissolution rates from copper covered with PPy-IP₆ and from bare copper during immersion for 900 h were approximately 0.096 and 1.8 µg cm⁻² h⁻¹, respectively. The dissolution rate of copper covered with the PPy-IP₆ film was inhibited by a factor of 1/19 relative to that of bare copper. Although the potential of copper covered with PPy-IP₆ fell to −0.05 V at 750 h, as shown in Fig. 2-6, the amount of copper ions dissolved was still relatively low, meaning that the PPy-IP₆ layer continued to protect against copper corrosion after 750 h of immersion in NaCl solution.

![Graph showing amount of dissolved copper over time](image)

**Fig. 2-7** Amount of Cu ions dissolved from bare copper and copper covered with the PPy-IP₆ layer during immersion in 3.5% NaCl solution. The PPy-IP₆ layer was formed in pH 6 phytic acid solution at 5.0 mA cm⁻² for 400 s. The amount of Cu ions dissolved from the unit surface area of the copper was calculated from the concentration analysed and the volume of electrolyte at 180 cm³.

2.3.3.3 Electrochemical impedance spectroscopy in 3.5% NaCl solution
Electrochemical impedance spectroscopy (EIS) provides valuable insight into corrosion mechanisms. The corrosion of the PPy-coated Cu electrode was studied by the EIS at the open circuit condition in 3.5 % NaCl solution. Fig. 2-8 shows EIS of PPy-coated copper in 3.5% NaCl solution after 1 h and after 24 h immersion. The EIS was drawn on the Nyquist plot (Fig. 2-8(A)) as well as the Bode plot (Fig. 2-8(B)). In Fig. 2-8, the plots simulated from an equivalent circuit described later were drawn. In Fig. 2-8(A), three characteristic frequency regions were observed. In the frequency region above 21.1 Hz, a semicircle appeared on the Nyquist plot. The intermediate frequency region of the spectra revealed a Warburg impedance, which increased with a slope of 45 deg. as the frequency decreased. The presence of Warburg impedance indicated that the film’s impedance included a diffusion process of electroactive species. In the frequency region below 50.1 mHz, the loci deviated on the upper side from the 45 deg. slope. When one will measure at frequencies lower than 10 mHz, which was the lowest limit in this study, a capacitive response will appear on the Nyquist plot. Several authors have reported the appearance of the capacitive response for the electroactive redox membrane in low frequencies [44-46]. The capacitance response has been assumed to be a pseudo capacitance, in which the redox species functioned as a charge accumulator. On the Bode plot in Fig. 2-8 (B), the response corresponding to the Nyquist plot was seen.
Fig. 2-8 EIS plot of copper covered with PPy-IP₆ in 3.5% NaCl solution (A) Nyquist plot and (B) Bode plots for 1 h; (C) Nyquist plot and (D) Bode plot for 24 h. PPy was formed from phytic acid solution at pH 6 by current density 5.0 mA cm⁻² for 400 s.

When the EIS after 24 h immersion was compared with that after 1 h immersion, the diameter of the semicircle in the high frequency region increased and the frequency region revealing the Warburg impedance decreased.

Fig. 2-9 shows the Nyquist plots of EIS after the longer immersion time than 24 h.
As shown in Fig. 2-9, each spectrum showed the same behaviour as those in Fig. 2-8. The diameters of the semicircle in the high frequency region increased with increase of the immersion time to approximately 1.3 kΩ cm² at 840 h immersion.

![Nyquist impedance plots](image)

**Fig. 2-9** Nyquist impedance plots of copper coated with PPy-IP₆ in 3.5% NaCl solution after 168 h immersion. PPy was formed from phytic acid solution at pH 6 by current density 5.0 mA cm⁻² for 400 s.

### 2.4 Discussions

#### 2.4.1 The structure of the PPy film on the copper surface

The chelating properties of phytic acid with metal ions greatly depend on the solution pH [27,30,47]. At approximately pH 6, H₆Phy⁶⁻ was stable and was expected to aid in corrosion inhibition by forming a compact IP₆-metal complex layer [47].

In this experiment, a high-concentration IP₆ solution was used as the electrolyte for the polymerisation of PPy. As shown in Fig. 2-2, on the potential transient for the polymerisation of PPy, an electric charge of 0.05 C cm⁻² flowed before the potential reached a peak. During the initial charge, we assume that Cu-IP₆ complex precipitates
on the copper surface according to the following equations:

\[ \text{Cu} \rightarrow \text{Cu}^{2+} + 2e^- \quad (2-2) \]

\[ \text{C}_6\text{H}_{12}\text{O}_{24}\text{P}_6^{6-} + n\text{Cu}^{2+} \rightarrow \text{Cu}_n(\text{C}_6\text{H}_{12}\text{O}_{24}\text{P}_6)^{(6-2n)^-} \quad (2-3) \]

The Cu-IP\textsubscript{6} complex layer is assumed to function as a passive layer to inhibit the dissolution of copper during the polymerisation of PPy. To confirm the formation of the Cu-IP\textsubscript{6} layer, the galvanostatic oxidation at 0.5 mA cm\textsuperscript{-2} was interrupted at 0.6 V in the initial stage (see Fig. 2-10(A)), and its surface was analysed by XPS and IR-RAS. In Fig. 2-10(B), the IR-RAS spectrum of the surface is shown. The absorption assigned to the phosphoric moiety in IP\textsubscript{6} was observed at 1004 and 1163 cm\textsuperscript{-1}. Comparing this spectrum to the absorption of phytate in Fig. 2-4(B), differences in peak position and intensity ratio are observed that may be attributed to the coordination of Cu ions to phytate. The XPS spectra in Fig. 2-10(C-E) provided another evidence. In the XPS spectra, a small peak of P2p\textsubscript{3/2} was observed, in addition to the peaks of C, O, and Cu (Fig. 2-10 (C)). The absence of an N peak indicated that PPy nucleation had not started at the potential of 0.6 V vs. SSE. In Fig. 2-10(D), the narrow scan spectra of P2p\textsubscript{3/2} is shown, because the peak in Fig. 2-10(C) was not clear. Fig. 2-10(E) shows the narrow-scan spectra of Cu 2p. The peaks at 932.5 and 952.5 eV corresponded to those of Cu 2p\textsubscript{3/2} and Cu 2p\textsubscript{1/2}, respectively. Along with the main peak at 932.5 eV, the shake-up satellite peaks were observed at high binding energy side, 942.5 and 943.9 eV. It was reported that the presence shake-up satellites was characteristics of partially filled d-band (3d\textsuperscript{9}) of Cu\textsuperscript{2+}, indicating the formation of Cu\textsuperscript{2+} salt [48]. A shoulder was observed at near of the main peak of Cu2p\textsubscript{3/2}. The shoulder
peak was associated to the Cu$^{2+}$ ions in cupric oxide. From the above observation, we can conclude that phytic acid forms a Cu(II)-complex layer on the copper surface before PPy nucleation begins. Thus, the nucleation of PPy may begin on the surface covered by the Cu(II)-IP$_6$ complex layer. The final structure after polymerisation is assumed to consist of the thin inner layer of Cu(II)-IP$_6$ and the relatively thick outer layer of PPy-IP$_6$.

**Fig. 2-10** (A) A potential transition of Cu during the PPy formation. The galvanostatic oxidation of copper in IP$_6$ solution containing Py monomer was interrupted at a potential of 0.6 V vs. SSE before the nucleation of PPy began. IR-RAS spectrum (B) and XPS spectra (C) of the copper surface. XPS narrow scan of P 2p$_{3/2}$ (D) and Cu 2p
2.4.2 EIS analysis

As shown in Figs. 2-8 and 2-9, the impedance response includes the R-C parallel circuit that corresponds to the semicircle in the high frequency region, the diffusion process in the intermediate frequency region, and the capacitive response in the low frequency region. The R-C parallel circuit may be a combination of the ionic charge transfer resistance (R_{i,ct}) with the double layer capacitance (C_{dl}) at the PPy/solution interface. From the diameter of the semicircle in Fig. 2-8 and 2-9, the R_{i,ct} value is found to increase with increase of the immersion time and the rate of the ionic transfer at the interface becomes smaller. From the diameter and the specific frequency at the top of the semicircle, we can determine the capacitance in the R-C parallel circuit. From Figs. 2-8 and 2-9, the capacitance is estimated to be about 10 \mu F cm^{-2}, which may be an appropriate value to the double layer capacitance at the PPy layer/ solution interface. With the decrease of frequency, the diffusion impedance appears on the impedance diagram. Several authors discussed the diffusion process in conducting polymer electrode [49-51]. C.R. Martin et al. [51] reported a semi-infinite diffusion mode in the PPy doped with exchangeable anions in the intermediate frequency region, in which the Warburg impedance was observed. When the frequencies are even lower, the growth of the diffusion length that is determined by the frequency is blocked by the real thickness of the PPy layer, and the finite diffusion length model can be applied. In the model, impedance behaves as a capacitance, i.e., pseudo-capacitance or redox capacitance.
From the impedance response in Figs. 2-8 and 2-9, we can draw several equivalent circuits, and, however, we choose a simple circuit of Fig. 2-11, in which the equivalent circuit was consisted of a parallel R-C circuit, a Warburg resistance and a redox capacitance.

**Fig. 2-11** Model and equivalent circuit of the Cu/PPy-IP$_6$ system. $R_{i\text{-ct}}$ is the ionic transfer resistance, $R_s$ is the solution resistance, $C_{dl}$ is the electric double layer capacitance, $C_{\text{redox}}$ is the redox capacitance of PPy film, and $W$ is the Warburg impedance of diffusion ions in the film.

From the equivalent circuit and the impedance response in Fig. 2-8, we simulated the values of the electric elements as a function of immersion time by using the software of ZSimpWin. The simulated impedance was well fitted with the experimental value in fitting error at a lever of $10^{-3}$. The values of $R_{i\text{-ct}}$, $C_{dl}$ and $C_{\text{redox}}$ simulated were plotted as a function of immersion time, and the results are shown in Fig. 2-12. The charge transfer resistance, $R_{i\text{-ct}}$, increases with immersion time. The increase of $R_{i\text{-ct}}$ may be induced by gradual degradation of the PPy layer, i.e., the rate of the ionic exchange process of the PPy layer with aqueous solution decreases with the immersion time. The double layer capacitance ($C_{dl}$) changed slightly with
immersion time in a range of 15-5 μF cm$^{-2}$. Redox capacitances with large values on the order of 10$^{-1}$ F cm$^{-2}$ were observed in Fig. 2-12. The large redox capacitance of the conducting polymer layer was also reported by Tanguy et al. [44,45]. The redox capacitance decreased as the immersion time increased, which may result from the gradual decay of the redox property of the PPy layer.

**Fig. 2-12** Change of electric elements $C_{dl}$, $R_{ct}$, and $C_{redox}$ in the equivalent circuit in Fig. 2-11 as a function of immersion time in 3.5% NaCl solution.

### 2.4.3 Corrosion protection by PPy film

From the amount of copper ions dissolved (Fig. 2-7), the dissolution in 3.5% NaCl solution of copper covered by the PPy-IP$_6$ was found to be smaller by 1/19, if compared with dissolution of the bare copper. The copper covered by PPy-IP$_6$ revealed high potentials at about 0.1-0.2 V, in which copper should be covered by the passive Cu$_2$O/ CuO film. At the high potential, the bare copper immersing in the NaCl solution was dissolved at much higher rate than that of the copper under natural
corrosion state [52-54]. The corrosion protection mechanism by the PPy film is not understood in detail at present and we can, however, introduce possible explanation on the mechanism. The oxidative property of the PPy-IP$_6$ causes the formation of the passive film that may consist of copper oxide or Cu-IP$_6$ complex. Further the PPy film works as a diffusion barrier of Cl$^-$ penetration. For the PPy doped with large size anions, the diffusion and migration of the doped ions have been reported to be much inhibited [55,56]. The PPy film in this case works as a cation-exchangeable membrane, in which cations can penetrate with the reduction of the PPy film to maintain the neutrality. We measured phosphorus ions during the immersion in 3.5% NaCl solution by ICP-AES. After the 800 h immersion, we detect no phosphorus ions higher than the detectable level. Little dissolution of phosphorus ion from the PPy film indicates that no exchange reaction between IP$_6$ doped in PPy and Cl$^-$ in aqueous solution takes place during the immersion and thus the penetration of Cl$^-$ is inhibited. The oxidative property inducing passivation of copper surface and the diffusion barrier against Cl$^-$ ions may play the large role of the PPy film to protect copper corrosion.

The protective and oxidative properties of the PPy-IP$_6$ film were degraded during the long immersion in the NaCl solution and finally potential was decreased to $-0.05$ V vs. SSE, as shown in Fig. 2-6. The degradation appears in the change of EIS during the immersion (Figs. 2-8, 2-9, and 2-12) in which the charge transfer resistance increased and the redox capacitance decreased gradually with the prolonging immersion. The both change may be related with the degradation of the oxidative
property of the PPy film. With the loss of oxidative property, the charge transfer at the PPy/solution interface becomes difficult and the amount of redox couple in the PPy film becomes small, corresponding to the decrease of the redox capacitance. The gradual degradation of the PPy-IP$_6$ film may be explained in the following way. With slow rate corrosion of copper from Cu to Cu$^{+/2+}$, the PPy matrix is gradually reduced.

\[
\text{Cu} \rightarrow \text{Cu}^{+/2+} + e \text{ or } 2e \quad (2-4)
\]

\[
\text{PPy}^{x+} + ye \rightarrow \text{PPy}^{(x-y)-} \quad (2-5)
\]

To maintain the neutrality, anions in the PPy film are dedoped or cations in aqueous solution are doped in the PPy film. As previously described, since there were little phosphorus ions in the solution after the long immersion, we can neglect the dedoping process of IP$_6$. Instead of the process, doping of cations, in this case, Na$^+$ ions into the PPy film occurs.

\[
\text{Na}^{+}_{\text{aq}} \rightarrow \text{Na}^{+}_{\text{(PPy)}} \quad (2-6)
\]

We can thus describe the reaction of the gradual degradation as the following.

\[
\text{PPy}^{x+-(x/6)\text{IP}_6^{6-} + y\text{Na}^{+}_{\text{aq}} + ye} \rightarrow \text{PPy}^{(x-y)+-(x/6)\text{IP}_6^{6-} - y\text{Na}^{+}} \quad (2-7)
\]

The loss of the oxidative property of the PPy film shifts the potential of the substrate copper in the less positive direction and causes a passive-to-active transition of the copper.

### 2.5 Conclusions

The following conclusions may be drawn from the present investigation.

(1) A uniform, compact and corrosion-resistant polypyrrole (PPy) coating was
synthesised on copper from phytic acid (IP$_6$) solution by constant current oxidation.

(2) A thin layer composed of Cu-IP$_6$ complex was initially formed, followed by the polymerisation and deposition of PPy doped with IP$_6$.

(3) The open circuit potential (OCP) of copper during the immersion in 3.5wt% NaCl solution was maintained in a high potential state for time periods longer than 800 h by the PPy-IP$_6$ coating.

(4) The dissolution rate of copper covered with a PPy-IP$_6$ layer was inhibited by a factor of 1/19 compared to that of bare copper.

(5) The PPy-IP$_6$ layer was degraded with the long immersion in 3.5% NaCl solution. The degradation was caused by loss of oxidative property of the PPy film. The change of the PPy film with prolonging immersion was seen in EIS response in which the charge transfer resistance and redox capacitance were increased and decreased, respectively, during the immersion.

2.6 References


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Chapter III

Influence of pH on the synthesis and properties of polypyrrole on copper from phytic acid solution for corrosion protection

3.1 Introduction

The corrosion protection of metals and alloys by using conducting polymer coatings has been reported by various authors. In 1985, Deberry [1] firstly reported that Polyaniline (PAni) layer could protect the stainless steel against corrosion in sulfuric acid solution. After that, different conducting polymers such as PAni [2], polythiophene (PT) [3], polypyrrole (PPy) [4,5], polyindole (PIn) [6] and Poly(o-phenylenediamine) (PoPD) [7], were then reported for the protection of corrosion. Among the conducting polymers, PPy is one of the most useful conducting polymers, because of its easy synthesis, high conductivity, biocompatibility and good environmental stability [8-10]. In the past decade, several papers have been reported for PPy films to protect the metals, such as, Fe [8,11-14], Al [15], Zn [16,17] and Cu [18,19]. In the previous part, we reported that the environmentally “green” reagent, phytic acid (IP₆), was effectively doped into the PPy film on copper and the PPy doped with IP₆ displayed a good stability and protective property against copper corrosion [20]. Since the ionization of the IP₆ as well as the complex formation of IP₆ with copper (Cu-IP₆) depend on the pH of the solution [21-23], it is assumed that the formation of PPy on copper depended on the pH of the Phytic acid solution.

In this part, we studied the effects of the pH as well as applied current density (CD)
on the PPy polymerization-deposition process on copper electrode. The morphology, conformation and corrosion-protection property of the PPy films were investigated.

3.2 Experimental

Pyrrole monomer (Py) was purchased from Tokyo Chemical. (99 wt.% purity), and used without further treatment. IP₆ aqueous solution at concentration of 50 wt.% and all the other reagents at analytical grade were purchased from Wako Pure Chemical Industry. The solutions used were prepared from double distilled and subsequently deionized Millipore water. The solution for electropolymerization of PPy was 0.1 mol dm⁻³ (M) IP₆ and 0.5 M Py. The pH of the solution was prepared in the range from 1 to 9 by addition of 1 M NaOH solution. Prior to the electrochemical experiments, the solutions were deaerated by bubbling high-purity nitrogen at least 15 min.

Pure copper (99.99 wt.%) 2 mm thick was cut into rectangular sheets (25 mm × 15 mm). The copper sheets were mechanically polished with #1000 SiC paper, then degreased with acetone, and washed with pure water. The sheet with an exposure area of 10 mm × 10 mm was used as working electrode for the PPy deposition, while the other surface was coated by silicon resin.

A three-electrode electrochemical cell with an approximate volume of 50 cm³ was used to perform the electropolymerization on copper. An Ag/AgCl/ Sat. KCl (SSE) was used as reference electrode and a platinum foil as counter electrode. All the potential in the paper was plotted vs. SSE, the potential of which was 0.197 V vs. SHE. The PPy polymerization and deposition were performed under constant current
control. The applied current density (CD) was changed in the range from 1 to 10 mA cm$^{-2}$.

Scanning electron microscope (SEM), JEOL JSM-6510LA, was used to study the surface morphology of the PPy film. The PPy film doped with phytate anions was analyzed by Raman spectroscopy (RS), and X-ray photoelectron spectroscopy (XPS). For Raman spectroscopy, a polychromatoric spectrometer (Bunko-Keiki M30-TP-M) was used and the excitation was made by YVO$_4$ solid-state laser beam at 532.0 nm wavelength. A highly sensitive CCD, Andor DO4041A, was used to detect the Raman scattering light. The laser power for the excitation was controlled to be lower than 5 mW to avoid damage to the PPy film. The XPS measurement was performed on a JEOL-9200 with an X-ray source of Mg K$\alpha$ at energy of 1253.6 eV. The XPS spectra were calibrated with the Au 4f $7/2$ peak at 84.00 eV. The Gaussian form was assumed in deconvolution of the spectrum, in which the full width at half maximum (FWHM) was kept constant for all components.

Adhesion strength of the PPy film to the copper substrate was measured by a sellotape test which consists in cutting the PPy film into small squares, sticking the tape and then stripping it. The ratio of the number of adherent film squares remaining to the total number gives the adherence strength in percentage.

The mass change of the copper electrode during PPy polymerization was monitored in-situ by electrochemical quartz crystal microbalance (EQCM) in which a frequency sensor, Maxtec KPS550 was coupled with a frequency counter, Advantest 5381. An Au coated AT-cut quartz crystal at 5 MHz resonance frequency mounted in the
frequency sensor was used as work electrode. The EQCM measurements were performed in a three-electrode cell with a volume of 250 cm$^3$. Before the PPy deposition, copper was electrodeposited on the Au coated quartz crystal at 24 mA cm$^{-2}$ for 360 s in a solution containing 0.5 M H$_2$SO$_4$ and 0.5 M CuSO$_4$. The copper layer at 2.8 mg cm$^{-2}$ was deposited on gold from the above electro-deposition and the thickness of the layer was estimated to be about 3 µm. From the copper deposition, the calibration of mass to frequency of EQCM was performed by assumption of 100% current efficiency of copper deposition. The ratio of the mass change ($\Delta m$) to the frequency change ($\Delta f$) was calibrated to

$$\Delta m = -K \Delta f$$ (3-1)

The value of $K$ was determined experimentally using Faraday’s law during copper deposition and evaluated at 28 ng cm$^{-2}$ Hz$^{-1}$.

The protective properties of the PPy formed on copper was examined by immersing the PPy-coated copper in an aqueous 3.5% sodium chloride solution at a temperature of 25 ± 1 °C under open-air condition. During the immersion, the open circuit potential (OCP) of the copper was monitored against SSE by a potentiometer, Hokuto-Denko HE104 and a data logger, Graphtec Midi Logger GL-450. The amount of copper ions dissolved in solution was measured by an inductively coupled plasma-atomic emission spectrometry (ICP-AES), Thermo-ICAP 6000.

Linear sweep voltammogram was measured in the NaCl solution by a Hokuto Denko HZ-5000 potentiostat in a glass cell with 100 cm$^3$ volume.
3.3 Results

3.3.1 Effects of pH and applied CD on PPy deposition

The PPy layer was formed in 0.1 M IP₆ solutions at pH from 1 to 9 containing 0.5 M pyrrole monomer (Py) at current densities (CDs) from 1 to 10 mA cm⁻².

Fig. 3-1 Potential change with time during electropolymerization of PPy films on copper from the phytic acid solution at different pH values at CD of (A) 1 mA cm⁻², (B) 5 mA cm⁻².

Fig. 3-1(A) and (B) show the potential-time curves for galvanostatic deposition of PPy in the IP₆ solution at various pH values at CD of 1 and 5 mA cm⁻². The potential-time curves largely depended on the pH of the solution. In the pH from 4 to 6, the potential transient was characterized by the two distinct stages except for the transient at CD = 1 mA cm⁻² in pH 4. At the first stage in the transient, the potential revealed a plateau, although the period and potential depended on the solution pH. At the end of the plateau, the potential gradually rose to a peak and then decreased to a steady value. Black PPy film started to form on copper at the potential peak. The first
plateau was assumed as an induction period of the electropolymerization of PPy and the following potential peak corresponded to the over-potential for the nucleation of PPy on copper. The period of the initial potential plateau was shorter with the higher pH value, as shown in Fig. 3-1(A) and (B).

![Figure 3-1](image-url)

**Fig. 3-2** The potential and mass change of the electrode during PPy formation in (A) pH 4, and (B) pH 5. In the figures, line (a) and (b) were the potential and mass change during PPy polymerization on copper, line (c) and (d) were the potential and mass change during PPy polymerization on Au, and line (e) the mass change of the copper electrode during Cu dissolution, if assumed that Cu was oxidized to Cu$^{2+}$.

The mass change of the copper electrode during PPy polymerization in the IP$_6$ solution at different pHs was monitored in situ by EQCM. Fig. 3-2(A) and (B) show the mass change of the copper electrode during PPy polymerization in the IP$_6$ solution at pH 4 and 5, respectively. For comparison, the mass change of the Au electrode during PPy deposition in the solution with pH 4 and 5 were also plotted in Fig. 3-2. Both in Fig. 3-2(A) and (B), the lines (a) and (b) indicate the potential and mass change of the Cu electrode during PPy polymerization, respectively, the lines (c) and
(d) indicate the potential and mass change of the Au electrode during PPy polymerization, respectively, and the line (e) was the mass change of the copper electrode due to the copper dissolution, if assumed that the copper was dissolved into Cu$^{2+}$. For the PPy formed in the phytate solution with pH 4, as shown in the curve (c) in Fig. 3-2(A), the mass of the Au electrode increased lineally as the function of charge pass once the current was applied to the Au electrode. When the PPy was deposited on copper, the mass of the copper electrode was changed in accordance with the stages as shown in the line (b) in Fig. 3-2(A). According to the first stage of potential in the line (a), the mass initially decreased as shown by the line (b) in Fig. 3-2(A) due to the dissolution of substrate. When one compared the line (b) and (e) in Fig. 3-2(A), it was found that a lower dissolution rate was observed at the first stage in the line (b). With the dissolution of copper, accumulation of Cu ion takes place to induce precipitation of salt layer. The low dissolution rate was induced by the precipitation of the Cu-IP$_6$ complex on the copper electrode. After the potential exhibited the peak, the mass of the electrode start to increase due to the PPy deposition and when the potential reached the stable plateaus, the mass was linearly increased as shown in the line (b) with the same slope of the line (d). Thus, in the period of the second potential plateaus, the current efficiency was assumed to be 100% and no side reaction took place. In Fig. 3-2(B), when PPy was formed in the IP$_6$ solution with pH 5, the mass (line (b)) initially reveals small plateau, then after a slight decrease responding to the potential peak, the mass increased linearly with charge, and the ratio of mass to charge is almost same as that on the gold.
**Fig. 3-3** Potential change with charge during electropolymerization of PPy on copper at different CDs from the phytic acid solution at (A) pH 4 and (B) pH 9.

The potential transient during the constant-current oxidation was also influenced by the CD applied. The effect of CD is seen in Fig. 3-3(A) and (B), in which the potential is plotted as a function of charge passed during constant current oxidation at CDs from 1 to 10 mA cm$^{-2}$ in the solutions at pH 4 and 9. In the pH 4 solution, the potential did not reach the second stage at CD lower than 2 mA cm$^{-2}$ and no black PPy layer was seen on copper. For the formation of the PPy layer, CD higher than 4 mA cm$^{-2}$ was required. In the pH 9 solution, the initial plateau disappeared and the potential rapidly increased to the maximum.

In the solutions at various pH values from 1 to 9, the PPy formation was examined under constant current control at CDs from 0.5 to 10 mA cm$^{-2}$. Table 3-1 summarizes the effects of the solution pH and applied CDs on the formation of the PPy layer. In the solution at pH 1, no polymerization and deposition of PPy occurred in the whole...
CDs. By contrast, the PPy layer was formed in the solutions at pH 6 and 9 even at the small CD of 0.5 mA cm$^{-2}$.

Table 3-1 The formation of PPy films in mixture solution of 0.1 M phytic acid and 0.5 M Py monomer at different applied current density and pH values.

<table>
<thead>
<tr>
<th>CD (mA cm$^{-2}$)</th>
<th>pH 1</th>
<th>pH 3</th>
<th>pH 4</th>
<th>pH 4.5</th>
<th>pH 5</th>
<th>pH 6</th>
<th>pH 9</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>1</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>2</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>4</td>
<td>×</td>
<td>×</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>5</td>
<td>×</td>
<td>×</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>10</td>
<td>×</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
</tbody>
</table>

× The potential does not rise to enough high potential to polymerize pyrrole.

✓ The PPy can be formed in the applied condition.

As shown in Fig. 3-1 and 3-3, the charge of the induction plateau was changed with the CDs applied and the pH of the solution. The charge decreased with increase of the both CDs and pH, and the change of the charge with CDs was seen more clearly in solution at the lower pH. For example, the charge for the induction plateau to the peak potential in the pH 4 solution in Fig. 3-3(A) decreased from 1.2 C cm$^{-2}$ at 4 mA cm$^{-2}$ to 0.3 C cm$^{-2}$ at 10 mA cm$^{-2}$. In the pH 5 solution, the charge changed from 0.2 C cm$^{-2}$ at 1 mA cm$^{-2}$ to 0.03 C cm$^{-2}$ at 5.0 mA cm$^{-2}$.
No obvious induction plateau was seen in the potential-charge curves in the alkaline solutions at pH 9, in which the potential during the PPy formation revealed relatively high value of about 4 V at the peak and 1 V in the second plateau. The high potential for PPy formation in alkaline solution was reported by Iroh et al. [14] and Ryu et al. [17].

3.3.2 Surface morphology of PPy film

The surface morphology of the PPy films formed at different conditions was observed by SEM. The SEM photographs are shown in Fig. 3-4, in which the PPy were formed in the phytic acid solution at pH 6 at CD of 5 mA cm$^{-2}$ (Fig. 3-4(A)); at pH 6 at 1 mA cm$^{-2}$ (Fig. 3-4(B)) and 5 mA cm$^{-2}$ (Fig. 3-4(C)). The charge of the PPy preparation in Fig. 3-3 was controlled at 2 C cm$^{-2}$. 
**Fig. 3-4** SEM morphology of the PPy films on copper formed under constant current in the phytic acid solution with different pH values. (A) I= 5 mA cm$^{-2}$ at pH 4; (B) I= 1 mA cm$^{-2}$ at pH 6, (C) I= 5 mA cm$^{-2}$ at pH 6.

As shown in Fig. 3-4, PPy films with cauliflower-like morphology were formed in the solutions at pH 4 and pH 6. In the cauliflower-like feature, small spherical grains with 2-5 µm diameters conglomerated. When one compared between the PPy formed in the solution at pH 4 (Fig. 3-4(A)) and at pH 6 (Fig. 3-4(B) and 3-4(C)), it was seen that the more smooth PPy film was prepared in the solution at pH 6. In addition, when one compared between SEM photographs in Fig. 3-4(B) and (C), the PPy layer with the smaller grain was formed at the smaller CD. We thus estimated that the more smooth and compact PPy film was prepared at the smaller CD. In the alkaline solution at pH 9, the continuous PPy film was similarly formed on copper surface and, however, it cracked after drying in air and easily peeled off from the surface.

For checking adhesion between the PPy film and the copper, the sellotape test is performed and the results are shown in Fig. 3-5. As shown in Fig. 3-5, for the PPy formed in pH 4 and 6 IP$_6$ solution, all parts of PPy film remained on the copper surface after the cellotape was peeled off (Fig. 3-5(A) and (B)). For the PPy film in the pH=9 IP$_6$ solution, however, only about one in three was remained on the substrate as shown in Fig. 3-5(C). The PPy films formed in the IP$_6$ solution with pH 4 and 6 are seen to be more adhesive.
3.3.3 Change in Raman spectra of the PPy film with solution pH

Fig. 3-6(A) shows Raman spectra of the PPy film formed on copper by constant current at CD = 5 mA cm$^{-2}$ in the solutions at pH 4, 6 and 9. The change of the Raman spectra of the PPy film with the CDs at 1, 5 and 10 mA cm$^{-2}$ is shown in Fig. 3-6(B), in which the polymerization was done in the pH 5 phytic acid solution.

The assignment of the Raman bands is following. The strongest Raman peak at 1587 cm$^{-1}$ arises from a mode of the conjugated C-C chain [24,25]. The peaks at 1372, 1324 and 1236 cm$^{-1}$ are related to the ring deformation [17,24,26,27]. The double peaks at 935 and 972 cm$^{-1}$ are attributed to the –C–H out-of-plane deformation. According to Furukawa et al. [25], the peak at 935 cm$^{-1}$ is responded to the quinoid form and the peak at 972 cm$^{-1}$ to benzoic form. The double peaks at 1057 and 1086 cm$^{-1}$ were due to the –N–H in-plane bending vibration [10, 26-29].

In Fig. 3-6(A), two bands at 1086 and 1372 cm$^{-1}$ disappeared in the PPy formed in
the alkaline phytate solution with pH 9. The Raman bands at 935, 972, and 1057 cm\(^{-1}\) of the PPy film formed in the pH 4 solution slightly changed to 940, 988, and 1046 cm\(^{-1}\), respectively, in the alkaline phytate solution. On the positively charged PPy matrix with bipolaron or dication state, the peak wavenumbers for \(-\text{N}–\text{H}\) vibration and the ring deformation were reported to be 1086 cm\(^{-1}\) and 1372 cm\(^{-1}\), respectively [24, 25]. In the weakly acidic solution at pH 4 and 5, it was seen that the bipolaron state existed on the PPy matrix and in the alkaline solution, however, there existed little amount of the bipolaron state from the absence of the both peaks.

In Fig. 3-6(B), the peak at 1086 cm\(^{-1}\) was not seen for the PPy formed at 1 mA cm\(^{-2}\) in the pH 5 solution. In addition, the intensity ratios of 935 cm\(^{-1}\) to 927 cm\(^{-1}\) peak and of 1057 cm\(^{-1}\) to 1086 cm\(^{-1}\) peak were changed with CD. As discussed later, the change of the intensity ratios was related to the oxidation degree of the PPy film.

![Raman spectrum diagram](image-url)
Fig. 3-6 (A) Raman spectra of the polypyrrole films formed in the IP₆ solution at different pH values at constant current 5 mA cm⁻², (B) Raman spectra of the polypyrrole films formed in the phytic acid solution at pH 5 at different CDs.

3.3.4 Change in XPS spectra of the PPy film with solution pH

The spectra of nitrogen changed with pH of the solution for preparation of the PPy film. Fig. 3-7 shows the N1s spectrum of the PPy film on copper. The nitrogen signal was deconvoluted into four peaks [30-33]. The main peak at 399.9 eV is attributed to the N atom (–N(H)–) in Py ring [30,34]. The two shoulders at higher energy was reported to correspond to positively charged nitrogen [34,35,36]; the shoulder 1.5 eV higher than the position of main peak was attributed to –N⁺(H)– in the polaron state of PPy, while the shoulder 3.0 eV higher was attributed to the more positively charged –N⁺(H)– in the bipolaron state ((–N⁺(H)–)ₙ). Another shoulder at the lower binding energy side (397.9 eV) can be defined as a structural defect in the form of imine-like nitrogen, –C=N– [33,37], which was assumed to be formed from dehydrogenation of pyrrollium nitrogen with the rearrangement of PPy bonds [34,35].
Fig. 3-7 The N1s XPS spectra of the PPy-IP₆ film on copper. PPy films were prepared at current 5 mA cm⁻² in the phytic acid solution at (A) pH 4, (B) pH 6, (C) pH 9.

For the PPy formed in alkaline solution, it was seen that the larger amount of imine-like nitrogen (≡C=N–) at 397.9 eV was contained in the PPy matrix than that in the acidic solution, probably due to strong nucleophile property of OH⁻ and higher potential for preparation of PPy shown in Fig. 3-3(B).

3.3.5 Corrosion protection of polypyrrole in NaCl solution

The corrosion of copper and its protection by the PPy films formed at different pH solution were evaluated by immersion in 3.5% NaCl solution, in which the open circle
potential (OCP) of the copper covered with the PPy films was recorded as a function of the immersion time. Simultaneously, the amount of copper ions dissolved during immersion was measured by ICP-AES. In Fig. 3-8(A) and (B), the OCP and the amount of copper ion were plotted as a function of the immersion time, respectively.

In Fig. 3-8, the PPy films were formed in the IP₆ solutions at pH 4 and 6 at 5 mA cm⁻² with a charge of 3 C cm⁻². The immersion test was not done for copper with the PPy film formed in the pH 9 solution, because of the poor adhesion and fragility of the film. As shown in Fig. 3-8(A), the OCP of bare copper decreased in the initial 100 h immersion and then remained approximately constant at −0.19 ± 0.01 V. For the PPy-coated copper, high potential at about 0.1–0.2 V was observed. The OCP continuously increased to the maximum value about 0.2 V at the initial 200 h. After that, the potential was kept at the value for several days and finally decreased to a value of −0.05 V. It was found that the copper covered with PPy formed in the pH 4 solution maintained the high potential state for the longer duration than the copper covered with PPy formed at pH 6. In addition, the better corrosion protection of the PPy film formed at the pH 4 solution was demonstrated from the amount of copper dissolved, as shown in Fig. 3-8(B). The average dissolution rate from the copper covered with the PPy-IP₆ films formed at pH 4 and pH 6 during 960 h immersion were about 1.6×10⁻⁸ g cm⁻² h⁻¹ and 1.0 ×10⁻⁷ g cm⁻² h⁻¹, respectively, both of which were much smaller than the average dissolution rate of 1.6×10⁻⁶ g cm⁻² h⁻¹ for bare copper.
Fig. 3-8 (A) Change of OCP of the copper covered with PPy and bare copper in 3.5% NaCl solution. (B) the amount of Cu ions dissolved during immersion of PPy-covered Cu and the bare copper. The PPy-IP₆ films were formed at CD of 5 mA cm⁻² for 600 s in phytic acid solution at pH 4 and 5. The amount of Cu ions dissolved from the unit surface area of the copper was calculated from the concentration analysed and the volume of electrolyte at 180 cm³.

Fig. 3-9 shows the photograph of the PPy-coated copper samples exposed in NaCl solution at different time. As shown in Fig. 3-9, for the bare copper, corrosion products was observed, when the copper was covered with PPy film formed in pH 4 IP₆ solution, no corrosion product was observed on the surface after 2 month immersion. However, for the copper covered with the PPy film formed in pH = 6 IP₆ solution, after 30 days immersion, a little of corrosion production was observed on the black surface. After 2 months immersion, more corrosion products were observed on the PPy film and the film was broken after it was dried in air.
Fig. 3-9 Photo graphology of the Cu covered with PPy films after the explosion at different time in NaCl solution.

To examine the protection mechanism, potential-current curve for the bare copper and the copper covered by the PPy film was measured by the linear potential sweep method at a sweep rate of 2 mV s⁻¹ in 3.5% NaCl solution under air-opened condition after the copper electrodes was immersed for 1 h. For comparison, the potential-current curve for the copper covered with Cu-IP₆ complex layer was also measured. The Cu-IP₆ layer was prepared by oxidizing the copper under constant CD of 5.0 mA·cm⁻² in pH 4 and 6 IP₆-Py solution to a potential of 0.3 V. The potential range for the measurement was in between \((E_{ocp} - 0.12)\) V and \((E_{ocp} + 0.3)\) V. The results were shown in Fig. 3-10. For the bare copper the corrosion potential was –0.2
V and the corrosion CD was estimated to be 2.1 μA cm\(^{-2}\) from extrapolation of the Tafel lines. When copper was oxidized in the IP\(_6\) solution at pH 4, the corrosion potential was shifted to –0.17 V and corrosion current of the copper was decreased to 1.0 μA cm\(^{-2}\) by the coating of Cu-IP\(_6\) layer, if compared with bare copper. And no obvious potential and current changes were observed for the copper oxidized in pH 6 IP\(_6\) solution. When the copper was covered with PPy, as shown in Fig. 3-10, the zero-current potential was seen to be shifted to the higher potentials by covering of the PPy film, and the exchange current densities was much increased, if compared with the bare copper. The exchange current density of the bare copper corresponds to its corrosion current and, however, for the PPy-covered copper, they represent those of the following redox property of the PPy on copper.

\[
\text{PPy}^{x+}(x/y)A^{y-} + ye^- \rightarrow \text{PPy}^{(x-y)+}(x-y)A^{y-} + A^{y-}_{aq} \quad (3-2)
\]

where \(A_{aq}^-\) represents doped anion. When we notice the anodic branch in the plot, the current of the bare copper or the copper oxidized in the IP\(_6\) solution is found to sharply increase and no passive region is observed. Probably the pitting corrosion was generated in the relatively low potential. By the PPy film covering copper, the anodic current is much suppressed.
Fig. 3-10 Potential-current curve for Cu/PPy (pH 4) ((a), ), Cu/PPy (pH 6) ((b), ), bare copper ((c), ), Cu-IP6 (pH 4) ((d), ), and Cu-IP6 (pH 6) ((e), ) in 3.5 % NaCl solution under air-opened condition. The Cu-IP6 layer was prepared by oxidizing the copper under constant CD of 5.0 mA·cm⁻² in pH 4 and 6 IP6-Py solution to a potential of 0.3 V. The curve was measured by the potential sweep from $E_{ocp} - 0.12$ V to $E_{ocp} + 0.3$ V vs. SSE at a sweep rate of 2 mV s⁻¹.

3.4 Discussions

3.4.1 Effect of pH on formation process of PPy film on copper
Fig. 3-11 Potential transients during electropolymerization of PPy film on copper at current 5.0 mA cm$^{-2}$ in the phytic acid solution at pH 4, 4.5 and 5.

When one oxidized the copper under galvanostatic condition in the acidic IP$_6$ solution containing Py monomer, we previously reported that a Cu(II)-IP$_6$ complex layer was initially formed on copper before the PPy nucleation [20]. The formation of the Cu-IP$_6$ was further confirmed by the EQCM results as shown in Fig. 3-2. At first we discuss the effect of the solution pH on the formation of the complex layer and its thickness. In the potential transient for PPy polymerization in the solutions at pH 4, 4.5 and 5, the polymerization of PPy was interrupted at a potential of 0.6 V, as shown in Fig. 3-11. The surface taken at the potentials were analyzed by XPS. Fig. 3-12 shows depth-profile of Cu2p$_{3/2}$ and P2p$_{3/2}$ signals measured by XPS with Ar ion sputtering. The sputtering condition was following: Pressure of Ar at 8.5 ×10$^{-4}$ Pa, voltage for acceleration of Ar$^+$ at 3 kV, and current of Ar$^+$ at 25 mA. In Fig. 3-12(A), the intensities of Cu2p$_{3/2}$ and P2p$_{3/2}$ signals gradually increased and decreased, respectively, during the 600 s sputtering and then sharply changed. We assume that
the depth profile at the initial 600 s corresponds to that of the complex layer of Cu-IP₆ on the surface treated in the pH 4 solution. The sputtering period corresponding to the complex layer became smaller at 300 s on the surface treated in the pH 4.5 solution. On the surface treated in the pH 5 solution, the initial sputtering region disappeared and the intensities sharply changed. The thickness of the PPy-IP₆ layer on the surface at pH 5 may be as thin as an absorption layer. When one compared the depth profile with the potential transient during the PPy formation in Fig. 3-12, the thickness of the PPy-IP₆ layer was assumed to be increased with the charge passed in the initial plateau. As shown in Fig. 3-3, since the initial plateau charge increased with the decrease of CD and the decrease of the solution pH, the thickness of the layer was assumed to be increased with the same manner. Although we did not know the sputtering rate of Cu-IP₆, considering the sputtering rate of SiO₂ at 4.36 nm per min, the thickness of the Cu-IP₆ complex layer was in the lever of several nanometers to several tens of nanometers.

During PPy formation, the current efficiency for the PPy formation decreased due to the initial substrate dissolution. According to the EQCM results in Fig. 3-2, the current efficiency for polymer formation was changed as a function of charge. Corresponding to the initial potential plateaus the mass change was related to copper dissolution and Cu-IP₆ precipitation, and after the potential exhibited the peak, the mass increased with charge, and the ratio of mass to charge is almost same as that on the gold. For easily estimating the current efficiency for the PPy formation, thus, we ignored the dissolution of substrate after the potential peak, and assumed that no side
reaction took place after the potential exhibited the peak. In Fig. 3-2, if the PPy was formed with charge of 2 C cm$^{-2}$, the current efficiencies for the PPy formation formed in the IP$_6$ solutions with pH 4 and 5 were estimated to be about 65 % and 98 %, respectively.

**Fig. 3-12** Depth profile of Cu2p$^{3/2}$ and P2p$^{3/2}$ XPS spectra. The copper electrode was taken after the interruption at 0.6 V vs SSE in Fig. 3-11.

From the intensity ratio of XPS signals of Cu and P in Fig. 3-12, the composition ratio of Cu to IP$_6$ in the surface layer may be derived from the calibration of the signals. The Cu/IP$_6$ molar ratio thus estimated was 4.9 in average at pH 4 and 6 at pH 4.5. The coordination number of Cu ions to IP$_6$ was reported to depend on the solution pH by several authors. Bebot-Brigaud et al. found that one molecule of Cu ion was
coordinated to IP$_6$ in the solution at pH 2 and multiple molecules were coordinated at higher pH from 4.5 to 9 [22]. Martin and Evans also evaluated the coordination number of Cu ion to IP$_6$ to be one at pH 2 and 6 at pH 6 [21]. They further suggested that when Cu ion was bound with IP$_6$ through the multiple coordination sites, the Cu-IP$_6$ complex could form a compact solid compound [21]. A possible mode proposed by Martin and Evans [21] for the Cu-IP$_6$ complex with binding of six Cu ions to the equatorial form of phytate was shown in Fig. 3-13.

![Diagram showing the structure of Cu-IP$_6$ complex](image)

\[ P = \text{O}^{-} \text{P} \equiv \text{O} \quad M = \text{divalent metal ion} \]

**Fig. 3-13** Schematic illustration of a possible structure for the binding of six metal ions to the equatorial form of phytate.

The PPy nucleation has started after the initial plateau, in which the Cu-IP$_6$ complex surface layer was formed. In the acidic solution at pH 1, however, copper underwent heavy dissolution and did not form any surface layer and the potential did not rise to a value high enough to start the polymerization of PPy. In the alkaline solution at pH 9, copper hardly dissolve and did not form the Cu-IP$_6$ complex layer.
PPy was directly deposited on copper surface. The instability of the PPy film formed in alkaline solution may originate from the lack of the intermediate complex layer.

3.4.2 Conformation change of PPy film with pH of solution for preparation

The Raman spectra (Fig. 3-6) and XPS N1s spectra (Fig. 3-7) exhibited small difference between the PPy films formed in the acidic and alkaline solution.

Fig. 3-14(A) shows the Raman spectra in the range of 800-1150 cm\(^{-1}\). The data in Fig. 3-14(A) is same as those in Fig. 6, but the horizontal axis is expanded. *Chen* et al. reported that the both peaks at 935 and 972 cm\(^{-1}\) were assigned to the –C–H out-of-plane deformation, and the peak at 935 cm\(^{-1}\) was responded to the oxidized state of PPy and the peak at 972 cm\(^{-1}\) to the neutral state [26]. The peaks at 1057 and 1086 cm\(^{-1}\) assigned to the –N–H deformation was also related to the oxidation degree; the peak at 1086 cm\(^{-1}\) was responded to the oxidized state and the peak at 1057 cm\(^{-1}\) to the neutral. The peak intensities of the individual pairs were estimated after the deconvolution by which the Gaussian shape was assumed at a half peak width of 35 cm\(^{-1}\). The ratios estimated were given in Table. 3-2, in which the ratios for the PPy layer formed was listed with the solution pH. The ratios of \(I_{935}/I_{972}\) and \(I_{1086}/I_{1057}\) decrease from 1.1 at pH 4 to 0.8 at pH 9 and from 0.87 to 0.25, respectively. The decrease of the ratio indicates that the oxidized state of PPy is decreased with the increase of pH.
Fig. 3-14 (A) Raman spectra of PPy in the range of 800–1150 cm\(^{-1}\) as a function of the solution pH for preparation. (B) Raman spectra of PPy in the range of 800–1150 cm\(^{-1}\) as a function of CDs for preparation of PPy.

Table 3-2 Ratios of Raman bands of 935 cm\(^{-1}\) peak to 972 cm\(^{-1}\) peak and of 1086 cm\(^{-1}\) peak to 1057 cm\(^{-1}\) peak as a function of solution pH. The PPy-IP\(_6\) films were formed in the phytic acid solution at constant current density 5 mA cm\(^{-2}\) for 600 s.

<table>
<thead>
<tr>
<th>Ratio</th>
<th>pH 4</th>
<th>pH 6</th>
<th>pH 9</th>
</tr>
</thead>
<tbody>
<tr>
<td>(I_{935/972})</td>
<td>1.1</td>
<td>1.05</td>
<td>0.8</td>
</tr>
<tr>
<td>(I_{1086/1057})</td>
<td>0.87</td>
<td>0.8</td>
<td>0.25</td>
</tr>
</tbody>
</table>

In Fig. 3-14(B) the Raman spectra of PPy formed at the pH 5 solution were plotted as a parameter of CD. The ratios of \(I_{935/972}\) and \(I_{1086/1057}\) are listed in Table. 3-3, in which the both ratios decreased with the decrease of CD, indicating a decrease of oxidized state of the PPy.

Table 3-3 Ratios of Raman bands of 935 cm\(^{-1}\) peak to 972 cm\(^{-1}\) peak and of 1086 cm\(^{-1}\) peak to 1057 cm\(^{-1}\) peak as a function of CDs for preparation of PPy.
peak to 1057 cm\(^{-1}\) peak as a function of CDs. The PPY-IP\(_6\) films were formed in phytic acid solution at pH 5.

<table>
<thead>
<tr>
<th>Ratio</th>
<th>1 mA cm(^{-2})</th>
<th>5 mA cm(^{-2})</th>
<th>10 mA cm(^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(I_{935}/I_{972})</td>
<td>0.9</td>
<td>1.05</td>
<td>1.15</td>
</tr>
<tr>
<td>(I_{1086}/I_{1057})</td>
<td>0.4</td>
<td>0.8</td>
<td>0.9</td>
</tr>
</tbody>
</table>

We confirmed the relation between the solution pH and the oxidation degree of PPY by XPS. As previously shown in Fig. 3-7, there were four types of nitrogen in the PPY film: \(=\text{N}^-\), \(-\text{N}(\text{H})^-\), \(-\text{N}^+(\text{H})^-\) and \((-\text{N}^+(\text{H})^-)_{\text{bi}}\), where \((-\text{N}^+(\text{H})^-)_{\text{bi}}\) indicates a positively charged nitrogen under the bipolaron state. According to Skotherim [38], the possible structures of the four type nitrogen were given in Fig. 3-15. The ratios of the four types of nitrogen measured by XPS are listed in Table 3-4, in which the ratio was calculated from the individual intensities of the peaks deconvoluted. The ratio of the charged nitrogen, \(-\text{N}^+(\text{H})^-\) and \((-\text{N}^+(\text{H})^-)_{\text{bi}}\) amounted to about 32\% and 29\% in the PPY formed in the solution at pH 4 and pH 6, respectively. A smaller ratio of the charged nitrogen was seen for the PPY formed in the alkaline solution at pH 9 and the ratio of \(=\text{N}^-\) was increased to 15\%. The larger amount of \(=\text{N}^-\) type structure in the alkaline solution was assumed to break the conjugated C–C chain in PPY matrix, resulting in degradation of the electric conductance.
Fig. 3-15 Schematic illustration of the possible structure for the four type of nitrogen in PPy strain.

Table 3-4 Ratios of the different nitrogen species in polypyrrole matrix formed in the phytic acid solution at pH 4.0, 6.0 and 9.0.

<table>
<thead>
<tr>
<th>Element state</th>
<th>Binding energy (eV)</th>
<th>pH 4.0 Components (%)</th>
<th>pH 6.0 Components (%)</th>
<th>pH 9.0 Components (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>−N=</td>
<td>398 ± 0.2</td>
<td>5.9</td>
<td>5.1</td>
<td>15.1</td>
</tr>
<tr>
<td>−N(H)−</td>
<td>399.9 ± 0.2</td>
<td>60.9</td>
<td>65.6</td>
<td>75.6</td>
</tr>
<tr>
<td>−N+(H)−</td>
<td>401.5 ± 0.2</td>
<td>27.7</td>
<td>23.6</td>
<td>8.3</td>
</tr>
<tr>
<td>(−N+(H)−)bi</td>
<td>402.7 ± 0.2</td>
<td>5.5</td>
<td>5.7</td>
<td>1.0</td>
</tr>
</tbody>
</table>

3.4.3 Effects of the pH on the corrosion protection of PPy films
Several mechanisms have been proposed about the protection of the conducting polymer against corrosion on metal [39, 40]. The widely accepted explanation is the anodic protection, in which the strongly oxidative property of the conducting polymer shifts the potential of metals to the positive direction, inducing metals to be passivated. In addition, the polymer coating works as a barrier against the penetration of oxidants and aggressive anions, protecting the substrate metals. As seen in Fig. 3-8 and 3-10, the copper was maintained at high potentials from 0.2 to 0.1 V for long time by the PPy-IP₆ film during the immersion in NaCl solution. In the potential region, copper may be covered by a passive oxide of Cu₂O/ CuO including Cu-IP₆ complex layer. When bare copper is immersed in NaCl solution, the passive oxide is broken down and a heavy corrosion is started. The PPy-IP₆ film must inhibit the penetration of aggressive Cl⁻ from the solution side.

For the corrosion protection, we believed that the PPy-IP₆ film plays a principle role and in addition, the inner thin layer of Cu-IP₆ complex might affect the protection performance of the polymer. A better protection property was found for the PPy-IP₆ film formed in the IP₆ solution at pH 4. The higher quality of corrosion protection is probably related to the presence of inner Cu-IP₆ layer, which acts as a physical barrier like the passive film to inhibit dissolution of the substrate copper. It was suggested in Fig. 3-12 that a relatively thick Cu-IP₆ layer was formed before PPy polymerization in the solution at pH 4. Another factor is the oxidative property of the PPy film. As shown in Tables 3-2 and 3-4, the higher oxidative PPy was formed in the pH 4 solution.
3.5 Conclusions

Polypyrrole (PPy) films have been formed on copper under constant current control in phytic acid solutions at various pHs to protect copper corrosion. The following conclusions were found.

(1) The oxidation degree of the PPy film depended on the solution pH for preparation, increasing with the more acidic solution. In the more acidic solution, the higher CD is required to form the PPy layer.

(2) A Cu-IP₆ complex layer was formed before the nucleation of PPy. The thickness of the Cu-IP₆ layer depended on the CD applied and solution pH. The thicker Cu-IP₆ layer was formed in the more acidic solution and at the lower CD.

(3) The PPy film prepared in the IP₆ solution at pH 4 inhibited copper corrosion in 3.5 wt.% NaCl solution most effectively. The PPy film inhibited copper corrosion at 1/100, if compared with that of the bare copper, and the inhibition continued for about 80 days.

3.6 References


Chapter IV

Electrochemical impedance spectroscopy and electrochemical quartz crystal microbalance to study the corrosion process of PPy-coated copper in aqueous solution

4.1 Introduction

Copper and its alloys are widely used because they offer high corrosion resistance. The copper and its alloys, however, suffer from heavy corrosion in environment including chloride ions. For use of copper in the seashore, the prevention of the corrosion of copper should be realized [1].

Many researchers have devoted attention to the corrosion protective properties of conducting polymer [2-5], since the first report using Polyaniline (PAni) for protection of the stainless steel in 1985 by Debbery [6]. The corrosion protection of copper by using conducting polymers has been reported by several authors. Fenelon and Breslin [7] electopolymerized a polypyrrole (PPy) coating on a copper-nickel alloy in neutral sodium oxalate solution. The coating exhibited a property of the corrosion protection in acidified and neutral NaCl solution. Tuken [8] electrochemically synthesized polyindile (Pln) which exhibited physical barrier behavior against the attack of corrosive environment and reduced the corrosion rate of copper. In addition, authors prepared conducting polymers on copper or copper alloy
from several acid medium such as, phosphoric acid [9], dodecylbenzenesulfonic acid [10] and salicylate acid [11] for corrosion protection. The polymers thus prepared, working as a physical barrier or passivator, protected the copper from dissolution in chloride-contained solution for periods from several hours to several weeks.

In the previous part we anodically synthesized a protective PPy film on copper from phytate (Phy or IP₆) solution [12]. It was found that the aqueous solution was a suitable medium for synthesizing uniform and strongly adherent PPy on copper. Further, we found that the formation and protection property of the PPy film depended on the pH of the solution and the PPy formed in the phytate solution at pH 4 exhibited highest corrosion-inhibition of copper in aqueous chloride environment [13].

In this part we investigated the protection mechanism of the PPy film doped with phytate anions (Phyⁿ⁻) by using electrochemical quartz crystal microbalance (EQCM) and electrochemical impedance spectroscopy (EIS) in aqueous chloride solution. The PPy doped with phosphate ions was also studied for comparison.

4.2 Experimental

Pyrrole (Py) monomer purchased from Tokyo Chemical Industries (99 wt.% purity) was used without any pre-treatment. Phytic acid solution was purchased in the form of aqueous solution at 50 wt.% concentration from Wako Pure Chemical. All other reagents at analytical grade were also purchased from Wako Pure Chemical. The solutions used were prepared from pure water doubly distilled followed by
purification by Mill-Q system.

Pure copper (99.99 wt.%) 2 mm thick was cut into rectangular sheets (25 mm × 15 mm). The copper sheets were mechanically polished with #1000 SiC paper, then degreased with acetone, and washed with pure water. The sheet with an exposure area of 10 mm × 10 mm was used as working electrode for the PPy deposition, while the other surface was coated by silicon resin.

For the PPy deposition on copper sheet, a three-electrode electrochemical cell with an approximate volume of 50 cm$^3$ was used. An Ag/AgCl/ Sat. KCl (SSE) was used as reference electrode and a platinum foil as counter electrode. All the potential in the paper was plotted vs. SSE, the potential of which was 0.197 V vs. SHE. Deposition of the PPy doped with Phy$^{n-}$ (PPy-Phy$^{n-}$) on copper was performed by constant current control at 5.0 mA cm$^{-2}$ from 0.5 M Py + 0.1 M Phy solution with pH= 4 [13], and the PPy doped H$_2$PO$_4^-$ (PPy-H$_2$PO$_4^-$) was deposited from 0.5 M Py + 0.1 M NaH$_2$PO$_4$ solution.

The mass change of the copper electrode during the PPy polymerization was monitored in-situ by an electrochemical quartz crystal microbalance (EQCM), in which a frequency sensor, Maxtec KPS550 was coupled with a frequency counter, Advantest 5381. An Au coated AT-cut quartz crystal with a 5 MHz resonance frequency mounted in the frequency sensor was used as the working electrode. The EQCM measurements were performed in a three-electrode cell with a volume of 250 cm$^3$. Before the PPy deposition, copper was electrodeposited on the Au coated quartz crystal in a solution containing 0.5 M H$_2$SO$_4$ and 0.5 M CuSO$_4$ at 24 mA cm$^{-2}$ for 360
A copper layer at 2.8 mg cm$^{-2}$ was deposited on gold from the above electro-deposition and the thickness of the layer was estimated to be about 3 µm. From the copper deposition, the calibration of mass to frequency of EQCM was performed by assumption of 100% current efficiency of copper deposition. The ratio of the mass change ($\Delta m$) to the frequency change ($\Delta f$) was calibrated to

$$\Delta m = -K\Delta f$$

(4-1)

$$K = 28 \text{ ng cm}^{-2} \text{ Hz}^{-1}$$

The potential-current relation of the copper covered by the PPy was measured in 3.5% NaCl solution under air-opened condition by linear potential sweep at a sweep rate of 2 mV s$^{-1}$ with a Hokuto Denko HZ-5000 potentiostat.

Electrochemical impedance spectroscopy (EIS) of the copper covered by the PPy was measured from $10^{-2}$ to $10^{4}$ Hz with 0.01 V$_{\text{rms}}$ amplitude by a frequency response analyzer (FRA), NF Circuit Design 5020, which was connected to a potentiostat specially designed in our laboratory.

For the study of the protective properties of the PPy film doped with Phy$^{n-}$ ions or H$_2$PO$_4^{-}$ ions, the copper covered by the PPy was immersed in an aqueous 3.5% sodium chloride solution under open-air condition. During the immersion, open circuit potential (OCP) was monitored against a SSE by a potentiometer, Hokuto-Denko HE104 and a data logger, Graphtec Midi Logger GL-450. The amount of copper ions dissolved in the solution was measured by an inductively coupled plasma-atomic emission spectrometry (ICP-AES), Thermo-ICAP 6000.

The surface morphology of the PPy film on copper was observed by a scanning
electron spectroscopy (SEM), JEOL JSM-6510LA and a confocal laser scanning microscopy (CLSM), Laser-Tech 1LD21D.

4.3 Results

4.3.1 Surface morphology of the PPy layers on Cu

The surface morphology of the PPy doped with Phy$^{n}$ (PPy-Phy$^{n}$) and PPy doped with H$_2$PO$_4^-$ anions (PPy-H$_2$PO$_4^-$) were observed by SEM and CLSM. Fig. 4-1(A) and (B) show the SEM photograph of the PPy-Phy$^{n}$ and PPy-H$_2$PO$_4^-$ on copper, respectively, and Fig. 4-1(C) and (D) show the three dimensional (3-D) CLSM view of the PPy-Phy$^{n}$ and PPy-H$_2$PO$_4^-$ films, respectively. Thickness of the PPy films was estimated from the cross-section SEM view inlet in Fig. 4-1(A) and (B). In Fig. 4-1(A), cauliflower morphology with different particle size from 2 to 10 µm diameters is observed for the PPy-Phy$^{n}$ film. The thickness of the PPy-Phy$^{n}$ film formed at 3 C cm$^{-2}$ was estimated 5.9 µm. A different morphology is observed for PPy-H$_2$PO$_4^-$ in Fig. 4-1(B), in which the PPy is agglomerated with smaller globule particle with a size of 0.1-1µm diameter. The thickness of the PPy-H$_2$PO$_4^-$ film formed at 3 C cm$^{-2}$ was estimated to be about 4 µm. From the 3-D CLSM-view in Fig. 4-1(C) and (D) we estimated the mean roughness of the PPy film surface ($Ra$). The arithmetical mean roughness ($Ra$) of the PPy-H$_2$PO$_4^-$ film surface was estimated to be 0.54 µm that was smaller than that of the PPy-Phy$^{n}$ film ($Ra= 0.81µm$).
4.3.2 Corrosion and corrosion protection in NaCl solution

The OCPs of the copper covered with the PPy-Phy$^{n^{-}}$ film (Cu/PPy-Phy$^{n^{-}}$) and the copper covered with the PPy-H$_2$PO$_4^{-}$ film (Cu/PPy-H$_2$PO$_4^{-}$) in 3.5% NaCl solution were monitored as a function of immersion time. The result is shown in Fig. 4-2, in which the OCP of the bare copper is also plotted for comparison. After an initial decrease, the OCP of the Cu/PPy-phy$^{n^{-}}$ increased to a range of 0.15 - 0.19 V, and the potential was then kept at constant potential for 1800 h. For the Cu/PPy-H$_2$PO$_4^{-}$, the OCP initially increased to its maximum value about 0.19 V at 100 h and then gradually decreased with the immersion time. After 700 h immersion, the OCP
reached $-0.05$ V. For bare copper, the OCP remained in the range of $-0.19$ to $-0.21$ V during the whole immersion.

Fig. 4-2 OCP of the copper covered by PPy-Ph\textsuperscript{h+}, and PPy-H\textsubscript{2}PO\textsubscript{4}\textsuperscript{-}, and barer copper during the immersion in 3.5 \% NaCl solution. The PPy films were prepared by constant current control at 5 mA cm\textsuperscript{-2} for 600 s.

During the immersion in 3.5 wt. \% NaCl solution, we measured the amount of Cu ions dissolved. The result is given in Fig. 4-3, in which the amount of Cu ions dissolved from the bare copper, Cu/PPy-H\textsubscript{2}PO\textsubscript{4}\textsuperscript{-}, and Cu/PPy-Ph\textsuperscript{h+}. For the Cu/PPy-Ph\textsuperscript{h+}, the concentration of Cu ions dissolved was less than detection limit in the initial 10 d immersion and the amount of Cu ion at 0.025 mg cm\textsuperscript{-2} was detected after 60 d immersion. For the Cu/PPy-H\textsubscript{2}PO\textsubscript{4}\textsuperscript{-}, trace amount of copper ions was detected after 1 d immersion, and the amount of copper ions gradually increased with the immersion time. During the 60 d immersion, the average dissolution rates from the Cu/PPy-Ph\textsuperscript{h+} and Cu/PPy-H\textsubscript{2}PO\textsubscript{4}\textsuperscript{-} were approximately 0.017 and 0.13 $\mu$g cm\textsuperscript{-2} h\textsuperscript{-1}, respectively, both of which were much smaller than that from bare copper at 1.7 $\mu$g cm\textsuperscript{-2} h\textsuperscript{-1}. The dissolution rates of copper from the Cu/PPy-Ph\textsuperscript{h+} and Cu/PPy-H\textsubscript{2}PO\textsubscript{4}\textsuperscript{-} were inhibited by a factor of 1/100 and 1/13, respectively, relative to that of bare
copper. Although the potential of the Cu/PPy-H_2PO_4^- decreased to –0.05 V at 700 h, as shown in Fig. 4-2, the amount of copper ions dissolved was still relatively low. The PPy-H_2PO_4^- film continued to protect the copper substrate after 700 h of immersion in the NaCl solution.

![Graph showing amount of dissolved copper ions over time](image)

**Fig. 4-3** Amount of Cu ions dissolved from copper covered with (A) PPy-Phy^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^
CuCl + Cl⁻ → CuCl₂²⁻ (4-3)

When the corrosion current density (CD) was calculated from the mass decrease by using the Faraday’s law with Cu dissolving as Cu⁺, the average dissolution CD was 2.2 µA cm⁻² for 40 h.

The mass changes of Cu/PPy-Phy⁻ and Cu/PPy-H₂PO₄⁻ were also measured during the immersion in the NaCl solution. The mass change of Au electrode covered with the PPy-Phy⁻ (Au/PPy-Phy⁻) and PPy-H₂PO₄⁻ (Au/PPy-H₂PO₄⁻) was measured for comparison. The results are plotted in Fig. 4-5(A) and (B) with the change of OCP. For Cu/PPy-Phy⁻, the OCP shifted to the negative direction in initial 5 h and then gradually increased, reaching a steady potential of about 0.12 V. The mass of the Cu/PPy-Phy⁻ in the NaCl solution increased by 42 µg cm⁻² in the 5 h immersion, and after the 40 h immersion the mass gain reached 59 µg cm⁻². The mass increase of the PPy-coated electrode may be related to the uptake of the water and ions from aqueous solution. Similar behavior of potential and mass change was seen for Au/PPy-Phy⁻ as
shown in Fig. 4-5(B).

**Figs. 4-5** Change of mass and OCP of Cu/PPy-Phy$^{n-}$ (A) and Au/PPy-Phy$^{n-}$ (B) in 3.5% NaCl. PPy film was formed in phytic acid solution at current density of 5.0 mA cm$^{-2}$ for 200 s.

**Fig. 4-6** Change of mass and OCP of Cu/PPy-H$_2$PO$_4^-$ (A) and Au/PPy-H$_2$PO$_4^-$ (B) in 3.5% NaCl. PPy film was formed in sodium dihydrogen phosphate solution at current density of 5.0 mA cm$^{-2}$ for 200 s.

For the Cu/PPy-H$_2$PO$_4^-$ the mass change and OCP were also measured. The results are shown in Fig. 4-6(A) and for comparison the results of the Au/PPy-H$_2$PO$_4^-$ are shown in Fig. 4-6(B). As shown in Fig. 4-6(A), The OCP of the Cu/PPy-H$_2$PO$_4^-$ initially decreased, accompanied by a gradual mass increase. Then the OCP was kept at steady potential of -0.05 V and the mass further increased to 32-34 µg cm$^{-2}$. The
Au/PPy-H₂PO₄⁻ electrode reveals slightly different behavior as shown in Fig. 4-6(B). The mass increase after 40 h immersion reached 40 µg cm⁻². The difference of the mass increase between Cu/PPy-H₂PO₄⁻ and Au/PPy-H₂PO₄⁻ is assumed to be caused by dissolution of copper substrate through the PPy film.

4.3.3 Potential-current relation

Fig. 4-7 Potential-current curve for Cu/PPy-Phy⁺, Cu/PPy-H₂PO₄⁻, and bare copper in a 3.5% NaCl solution under an air-opened condition. The curves were measured by potential sweep from $E_{ocp} - 0.12$ V to $E_{ocp} + 0.30$ V at a sweep rate of 2 mV s⁻¹. PPy film was formed at current density of 5.0 mA cm⁻² for 600 s.

Potential-current curves of the bare copper, Cu/PPy-Phy⁺, and Cu/PPy-H₂PO₄⁻ were measured in the 3.5% NaCl solution and shown in Fig. 4-7. The potential range for the potential-current measurement was restricted in between $(E_{ocp} - 0.12)$ V and $(E_{ocp} + 0.3)$ V to avoid large changes in the redox property of the PPy layer during the measurement. For the bare copper the corrosion potential was −0.2 V and the corrosion CD was estimated to be 2.0 µA cm⁻² from extrapolation of the Tafel lines.
The value is comparable to the corrosion CD at 2.2 µA cm$^{-2}$ estimated from the EQCM measurement in Fig. 4-4. In the anodic branch, the CD of the bare copper sharply increased to 100 µA cm$^{-2}$ at $-0.16$ V and no passive region was observed. Different behaviors are observed for the Cu/PPy-Phy$^{n-}$, and Cu/PPy-H$_2$PO$_4^-$ in Fig. 4-7. The zero-current potentials were shifted to 0.03 V for the Cu/PPy-H$_2$PO$_4^-$ and to $0.16$ V for the Cu/PPy-Phy$^{n-}$. The high zero-current potential indicates that the copper is oxidized by the PPy film which functions as an oxidant. The higher exchange CDs estimating from the extrapolation of the Tafel lines for the Cu/PPy-Phy$^{n-}$, and Cu/PPy-H$_2$PO$_4^-$ do not correspond to the corrosion CD of the copper substrate, but to the redox CD of the oxidative PPy film. Between PPy-Phy$^{n-}$ and PPy-H$_2$PO$_4^-$, the more positive zero-current potential and higher exchange CD were seen for the Cu/PPy-Phy$^{n-}$ in Fig. 4-7. The higher CD of the PPy-Phy$^{n-}$ indicates the higher redox activity of the PPy film. The real corrosion CD of the copper covered with the PPy layer is considered to remain smaller than that of the bare copper.

4.3.4 Mass change during the rodox reaction of the PPy film

For the rodox reaction of the conducting PPy film, doping behavior is assumed to be changed, depending on the property of the PPy film and doping anions. When the anions doped are relatively small in mass and volume, they are easily mobile in the PPy. Oxidation and reduction of the PPy are accompanied by doping of the anions from the electrolyte solution and dedoping to the solution, respectively.

$$\text{PPy}^{m+}(m/n)\text{A}^{-n} + xe^- \leftrightarrow \text{PPy}^{(m-x)+}(m-x/n)\text{A}^{n+} + (x/n)\text{A}^{-n}\text{(solution)} \quad (4-4)$$
When the anions doped are large in mass and volume and thus their mobility is small, the oxidation and reduction of the PPy are accompanied by dedoping of cations to the electrolyte solution and doping to the solution, respectively.

$$PPy^{n+(m/n)A^{n-}} + xM^{+}_{\text{solution}} + xe^{-} \leftrightarrow PPy^{(m-x)+}(m/n)A^{n+} xM^{+}$$  \hspace{1cm} (4-5)

In this case, mobile ions in the PPy should be particles positively charged or cations and the transfer particles at the interface of PPy film/aqueous solution are changed to cations. It influences the protection property of the conducting PPy whether the particles transferred at the interface are anions or cations. When the anions transfer at the interface and mobilize in the film, aggressive chloride ions are penetrated into the substrate copper and induce corrosion of the copper. On the contrary, when the cations are mobile particles, chloride attack may be avoided. For understanding the ionic exchange process, the mass change of the PPy film on Au was measured during the oxidation and reduction of PPy by EQCM.

**Fig. 4-8** Mass change during potential cycle of (A) Au/PPy-Phy$^{n-}$, and (B) Au/PPy-H$_2$PO$_4^{-}$. The potential scan rate was 5 mV s$^{-1}$ and PPy film was formed at current density of 5.0 mA cm$^{-2}$ for 200 s.

Fig. 4-8(A) and (B) show the mass changes of the Au/PPy-Phy$^{n-}$ and
Au/PPy-H$_2$PO$_4^-$ film, respectively, during cyclic oxidation and reduction. The data in Fig. 4-8 represents the mass change at the 16$^{th}$ cycle. Opposite behavior was seen between Au/PPy-Phy$^{n-}$ and Au/PPy-H$_2$PO$_4^-$. For the Au/PPy-Phy$^{n-}$, a mass increase was seen as shown in Fig. 4-8(A) during the cathodic scan and a decrease during the anodic scan. On the contrary mass decrease and increase took place for the Au/PPy-H$_2$PO$_4^-$ during cathodic and anodic scan, respectively. The mass change indicates that cation doping and dedoping occur for the Cu/PPy-Phy$^{n-}$ during the scans according to reaction (4-5) and anion dedoping and doping occur for the Cu/PPy-H$_2$PO$_4^-$ according to reaction (4-4). In other words, sodium ions and chloride ions are transferred at the PPy/electrolyte interface and migrated in the PPy film for the Cu/PPy-Phy$^{n-}$ and Cu/PPy-H$_2$PO$_4^-$, respectively.

4.3.5 EIS measurements

For understanding the process of corrosion and corrosion protection of copper covered with PPy during the immersion in 3.5% NaCl solution, electrochemical impedance spectroscopy (EIS) was measured at the OCP in the solution.

The EIS results at the immersion time of 1 h are given in Fig. 4-9 in which the EIS results of the bare copper (Fig. 4-9(A)), Cu/PPy-Phy$^{n-}$ (Fig. 4-9(B) on the Nquist plot and Fig. 4-9(C) on the Bode plot), and Cu/PPy-H$_2$PO$_4^-$ (Fig. 4-9(D) on the Nquist plot and Fig. 4-9(E) on the Bode plot) are plotted.

As shown in Fig. 4-9(A), EIS of the bare copper consisted of a semicircle in high frequency region responding to a couple of charge transfer resistance and electric double layer capacitance, and a Warburg diffusion element at low frequency region.
The charge transfer resistance determined from the diameter of the semicircle was in the level of $10^3 \, \Omega \, \text{cm}^2$ which was similar to those reported in previous reports [9,18]. The diffusion corresponds to that of $O_2$ in the solution. The similar impedance response of bare copper in NaCl solution has been reported in literatures [9,18] in which corrosion of copper was controlled by a diffusion process and the EIS data was fitted to a simple Randles-like circuit shown in Fig. 4-10(A).
**Fig. 4-9** EIS after 1 h immersion in 3.5% NaCl. (A) Nyquist plot of bare copper, (B) Nyquist plot of Cu/PPy-Phy\textsuperscript{n} and (C) Bode plot of Cu/PPy-Phy\textsuperscript{n}, (D) Nyquist plot of Cu/PPy-H\textsubscript{2}PO\textsubscript{4}\textsuperscript{−} and (E) Bode plot of Cu/PPy-H\textsubscript{2}PO\textsubscript{4}\textsuperscript{−}. The PPy film was formed at current density of 5.0 mA cm\textsuperscript{−2} for 600 s.

The EIS of the Cu/PPy-Phy\textsuperscript{n} in Fig. 4-9(B) and (C) was composed of a semicircle in high frequencies region and a diffusion impedance in low frequencies. The diffusion impedance responded to the diffusion of electro-active species in the PPy film. The slope of the diffusion element on the Niquist plot changes from 0.5 to the higher value with the lower frequency, though the lowest frequency limit of 0.01 Hz in this study is not enough to detect the behaviour. The equivalent electric circuit to the EIS in Fig. 4-9(B) and (C) is shown in Fig. 4-10(B). The semicircle in the higher frequencies represents the ionic charge transfer connected to the electric double layer at the PPy/electrolyte interface. The redox capacitance representing the redox property of PPy can appear when the diffusion length expanding with the lowering frequency reaches the real thickness of the PPy film.

The EIS of the Cu/PPy-H\textsubscript{2}PO\textsubscript{4}\textsuperscript{−} in Fig. 4-9(D) and (E) consisted of two semicircles. The semicircle in the frequencies lower than 21 Hz was not completed. The equivalent circuit to the EIS in Fig. 4-9(D) and (E) is shown in Fig. 4-10(C). The semicircle in the higher frequencies in Fig. 4-9(D) is related to the parallel connection of ionic charge transfer resistance and electric double layer capacitance at the PPy/electrolyte interface similarly as the circuit for the Cu/PPy-Phy\textsuperscript{n}, and the other
A semicircle in the lower frequency may be related to parallel connection between ionic resistance across the film and the redox capacitance of the polymer.

**Fig. 4-10** Nyquist plot of copper covered with (A) PPy-Phy\(^{n-}\) film or (B) PPy-H\(_2\)PO\(_4\)\(^{-}\) in NaCl solution as a function of immersion time. PPy film was formed at current density of 5.0 mA cm\(^{-2}\) for 600 s.

To study the corrosion protection and its degradation of the PPy film in the NaCl solution, the EIS of PPy-covered copper was measured during the immersion in the NaCl solution. Fig. 4-11(A) and (B) show the EIS results on the Nyquist plots of the Cu/PPy-Phy\(^{n-}\) and Cu/PPy-H\(_2\)PO\(_4\)\(^{-}\), respectively, as a function of immersion time in 3.5% NaCl solution. Using the equivalent circuits in Fig. 4-10(B) and (C), we simulated individual elements from EIS data in Fig. 4-11(A) and (B), respectively. The values of the elements estimated are listed in Table 4-1 for the Cu/PPy-Phy\(^{n-}\) and Table 4-2 for the Cu/PPy-H\(_2\)PO\(_4\)\(^{-}\).
Fig. 4-11 Equivalent circuits of (A) bare copper, (B) Cu/PPy-Phy\textsuperscript{b-} and (C) Cu/PPy-H\textsubscript{2}PO\textsubscript{4}\textsuperscript{−}. $R_{ct}$ is the charge transfer resistance, $R_{i-ct}$ is the ionic charge transfer resistance, $R_s$ is the solution resistance, $C_{dl}$ is the electric double layer capacitance, $R_p$ is the resistance of the PPy film, $C_{redox}$ is the redox capacitance of PPy film, and $W$ is the Warburg impedance for diffusion ions in the film.

Table 4-1 Electric elements of the equivalent circuit for Cu/PPy-Phy\textsuperscript{b-} simulated as a function of the immersion time in 3.5% NaCl solution.

<table>
<thead>
<tr>
<th>Time</th>
<th>$R_s$ (Ω cm$^2$)</th>
<th>CPE $C_{dl}$ (F cm$^2$)</th>
<th>$R_{i-ct}$ (Ω cm$^2$)</th>
<th>$C_{redox}$ (F cm$^2$)</th>
<th>W (Ω cm$^2$s$^{-1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 h</td>
<td>8.6</td>
<td>3.1E-6</td>
<td>41.5</td>
<td>9.0E-3</td>
<td>244</td>
</tr>
<tr>
<td>24 h</td>
<td>8.4</td>
<td>6.7E-6</td>
<td>93.4</td>
<td>3.0E-3</td>
<td>97</td>
</tr>
<tr>
<td>120 h</td>
<td>8.4</td>
<td>6.5E-6</td>
<td>139.2</td>
<td>4.3E-4</td>
<td>42</td>
</tr>
<tr>
<td>240 h</td>
<td>8.2</td>
<td>8.6E-6</td>
<td>471.5</td>
<td>3.4E-4</td>
<td>893</td>
</tr>
</tbody>
</table>

Table 4-2 Electric elements of the equivalent circuit for Cu/PPy-H\textsubscript{2}PO\textsubscript{4}\textsuperscript{−} simulated as a function of the immersion time in 3.5% NaCl solution.

<table>
<thead>
<tr>
<th>Time</th>
<th>$R_s$ (Ω cm$^2$)</th>
<th>CPE $C_{dl}$ (F cm$^2$)</th>
<th>$R_{i-ct}$ (Ω cm$^2$)</th>
<th>$C_{redox}$ (F cm$^2$)</th>
<th>$R_p$ (kΩ cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 h</td>
<td>10.8</td>
<td>6.5E-6</td>
<td>196</td>
<td>5.3E-4</td>
<td>41.6</td>
</tr>
<tr>
<td>24 h</td>
<td>11.1</td>
<td>8.5E-6</td>
<td>231.4</td>
<td>5.1E-4</td>
<td>26.1</td>
</tr>
<tr>
<td>120 h</td>
<td>12.0</td>
<td>8.1E-6</td>
<td>225.6</td>
<td>4.7E-4</td>
<td>13.4</td>
</tr>
<tr>
<td>240 h</td>
<td>12.3</td>
<td>8.0E-6</td>
<td>225.9</td>
<td>3.3E-4</td>
<td>10.8</td>
</tr>
</tbody>
</table>
4.4 Discussion

4.1 Water penetration into the PPy film

When PPy was immersion in the electrolyte solution, the water and ions is taken in the polymer from the solution, resulting in the mass gain. As shown in Figs. 4-5(B) and 4-6(B), mass of the Au/PPy-Phy\(^{a+}\) and Au/PPy-PPy-H\(_2\)PO\(_4\)\(^{-}\) increased initially and then reach a stable value after 20 h immersion in aqueous NaCl solution. In the 40 h immersion, the mass of the Au/PPy-Phy\(^{a+}\) and Au/PPy-H\(_2\)PO\(_4\)\(^{-}\) increased by 59 and 40 µg cm\(^{-2}\), respectively. Because the mass change induced by ion exchange shown in Fig. 4-8 was much smaller as compared with the total mass of the PPy film, the mass gain during the immersion may be caused by water penetration into the PPy film. The volume ratio of water penetrated to the PPy film was estimated by the following.

\[
P\% = \frac{\Delta m}{\rho \cdot d_{PPy}} \times 100\% \quad (4-6)
\]

in which \(\Delta m\) is the mass gain at 40 h immersion, \(\rho\) is the density of water, and \(d_{PPy}\) is the thickness of the PPy film formed at 5 mA cm\(^{-2}\) for 200 s. The \(d_{PPy}\) of the PPy-Phy\(^{a+}\) and PPy-H\(_2\)PO\(_4\)\(^{-}\) was measured to be about 1.9 and 1.3 µm, respectively. The calculation indicates that water penetrates into the PPy-Phy\(^{a+}\) and PPy-H\(_2\)PO\(_4\)\(^{-}\) film by a volume ratio of 3.1% and 3.0%, respectively, in the initial 40 h immersion. Probably the PPy film swells with the water penetration.

4.4.2 Corrosion protection by conducting PPy
From the amount of copper ions dissolved (Fig. 4-3), the dissolution of copper was much inhibited by the PPy-Phyₙ⁻ film and PPy-H₂PO₄⁻ film. For the corrosion protection by the conducting polymer film, two mechanisms were proposed; anodic protection and physical barrier effect [19]. On the former mechanism, the oxidative action of the polymer film induces passivation of the substrate metal and the passive state of the metal is kept under a state of a low rate of dissolution. Under the passive state, the metal is covered with a thin oxide or salt layer underneath the polymer film. On the latter mechanism, the polymer film works as a barrier against the penetration of oxidants and aggressive anions, protecting the substrate metals. We assume that the former mechanism of the anodic protection is preferential. Because the redox potential of the PPy film is significantly more positive than that of the corrosion potential of the bare copper, the OCP of the copper covered with PPy is shifted to the more positive potential than the OCP of the bare copper, as shown in Figs. 4-2 and 4-7. The potential shift induces the passivation of copper and may facilitate the formation of a passive oxide on the copper. The oxidative property of PPy further allows the oxide to be stably maintained.

We assume that the ionic perm-selectivity of the PPy film play a large role of the corrosion protection. From the EQCM measurement during the cyclic potential scan, as shown in Fig. 4-8, we proposed that the cation doping and dedoping occurred for the Cu/PPy-Phyₙ⁻ and the anion dedoping and doping for the Cu/PPy-H₂PO₄⁻ during the reduction-oxidation cycle. This means that the PPy-Phyₙ⁻ film possesses cationic perm-selective property and the PPy-H₂PO₄⁻ film anionic perm-selective property.
The cationic perm-selectivity of the PPy-Phy$^{b-}$ film inhibits penetration of chloride ion to the substrate and the chloride attack to the passive oxide. Cu/PPy-Phy$^{b-}$ thus maintains the passive state without dissolution of copper for the longer period than two months (Fig. 4-2). Cu/PPy-H$_2$PO$_4$ with the anionic perm-selectivity does not inhibit the penetration of the chloride ion to the substrate. The chloride ions reaching the copper substrate destroys the surface passive oxide and starts the corrosion dissolution of copper in the shorter time period than the period of Cu/PPy-Phy$^{b-}$.

4.4.3 Degradation of the PPy film

The corrosion protection of the PPy layer was gradually degraded and after long immersion in 3.5% NaCl solution, the corrosion and dissolution of the substrate copper was started. We discuss the origin of the degradation of the PPy films for corrosion protection in the following. As shown in Figs. 4-5 and 4-6, the mass of the PPy film was increased during the immersion in the NaCl solution. The OCP was initially changed to the negative direction and after the 4-5 h immersion, potential to the positive direction. The mass steadily increased irrespective the direction of OCP. We assumed that the mass increase was related to water permeation in the PPy film. With the water permeation, phytate (Phy or IP$_6$) anions doped in the PPy layer may be decomposed by hydrolysis reaction to form inositol penta- (IP$_5$), tetra- (IP$_4$), and tri-phosphate (IP$_3$), and, finally, phosphate [20,21]. The decomposed species in the PPy film with smaller mass and volume may change the ionic perm-selectivity of the PPy-Phy$^{b-}$ film from cationic to anionic and then facilitate the penetration of chloride
ions from the aqueous solution to the copper substrate. PPy doped with small anions can easily undergo simultaneous reduction and dedoping of anions to the aqueous solution. The gradual reduction of PPy occurs simultaneously with the water permeation during the long immersion, accompanied by oxidation from copper metal to copper ions.

\[
\text{Cu} \rightarrow \text{Cu}^{+2} + e/2e \quad (4-7)
\]

\[
\text{PPy}^{x+} + ye \rightarrow \text{PPy}^{(x-y)e} \quad (4-8)
\]

The reduction of the PPy takes place, resulting in the negative shift of the OCP in Fig. 4-2. When the PPy film was finally reduced to a neutral form, PPy film works only as a barrier against the penetration of oxidants and aggressive anions and loses a role of anodic protection.

With the mass increase, the EIS simultaneously changed, as shown in Fig. 4-11, and Tables 4-1 and 4-2. The ionic charge transfer resistance was increased with the immersion time and the redox capacitance was decreased. We assume that the both changes are related to the degradation of the PPy film. With increase of water permeated in the PPy film and gradual reduction of PPy, the redox property of the PPy film is weakened, resulting in decrease of the ionic charge transfer rate at the PPy/electrolyte interface, \textit{i.e.}, the increase of charge transfer resistance, and decrease of amount of available redox charge, \textit{i.e.}, the decrease of the redox capacitance. The weakening redox property of the PPy film with the immersion becomes difficult to keep the copper in the potential high enough to maintain passive state. Finally potential of the copper shifts in active region and starts corrosion of the copper.
4.5 Conclusion

Polypyrrole (PPy) films were prepared on copper in aqueous solution of sodium di-hydrogen phosphate and phytate (Phy) solution. The PPy films shift the open circuit potential (OCP) to passive state. The PPy film doped with Phy\textsuperscript{an} anions (PPy-Phy\textsuperscript{an}) working as the cationic perm-selective membrane effectively inhibits penetration of chloride ions to the PPy film. The copper covered with PPy-Phy\textsuperscript{an} was maintained in passive state for the longer period than 2 months in which dissolution of the copper were inhibited by 1/100 relative to that of bare copper. The copper covered with PPy-H\textsubscript{2}PO\textsubscript{4}\textsuperscript{−} film prepared in sodium di-hydrogen phosphate solution and possessing anionic perm-selectivity was inhibited by 1/13. The degradation of the PPy films was examined by EIS and mass change during immersion.

4.6 References


Chapter V

Effect of benzotriazole (BTA) addition on Polypyrrole film formation on copper and its corrosion protection

5.1 Introduction

Conducting polymers have attracted considerable attention due to their potential applications in batteries [1,2], electrochromic devices [3], sensors [4], electrocatalysis [5], and corrosion protection [6]. Among the conducting polymers, Polypyrrole (PPy) has been extensively investigated because of its ease of synthesis, high conductivity, biocompatibility, and good environmental stability [7]. Several papers have been reported on utilization of PPy to improve corrosion protection with copper [8-16]. The deposition of PPy on copper was reported in oxalic acid [9], phosphoric acid [11], phytic acid [12], salicylate acid [14], dodecylbenzene sulfonic acid [15], and sodium saccharin [16] solutions. Fenelon and Breslin [8] presented a PPy coating formed in oxalate media reducing the copper corrosion rate in neutral solutions. With acidic mediums for the PPy deposition, the oxidation of copper occurs before the pyrrole (Py) monomer is oxidized. When the polymeric PPy film grows with the formation of copper oxide, it was reported that the deposited PPy became less homogeneous and less adherent [17]. For the formation of homogenous and adherent PPy films, pretreatment of the copper substrate such as by surface passivation [17,18] and formation of a self-assembled organic layer [19] prior to the PPy
electropolymerization has been reported. Benzotriazole (BTA) is known as an effective corrosion inhibitor for copper and its alloys in aqueous solutions, and is widely used in industry [20,21]. In solutions containing BTA a protective Cu(I) BTA layer is rapidly formed on copper and copper alloy surfaces [22]. The protective layer thus formed is expected to hinder dissolution of the copper and enable the Py monomer to be easily electro-polymerized. Further, when BTA is included in the PPy matrix, the self-healing properties of the PPy layer may be enhanced.

In this part, BTA was introduced into a solution for PPy polymerization. Before the PPy deposition, a protective BTA layer was formed on the copper by immersion in an oxalic acid-Py (Ox-Py) solution containing BTA. Then the PPy deposition was performed on the copper. The effects of the pretreatment by BTA on the electropolymerization and corrosion performance of the PPy film were investigated.

5.2 Experimental

Pyrrole monomer purchased from Tokyo Chemical Co. (99 wt.% purity) was used without any pretreatment. All solutions were prepared from analytical grade reagents and pure de-ionized water obtained from a Millipore purification system.

Pure copper (99.99 wt.%) in rectangular sheets (25 mm × 15 mm) was used as the working electrode. The surface of the copper was sequentially polished with #220, 400, 600, 800, and 1200 SiC paper, degreased with acetone and ethanol, and finally washed with pure water. The exposed surface was 15 × 10 mm² and the rest of the
surface was covered by silicone resin.

For the PPy formation on the copper surface, an oxalic acid aqueous solution at 0.1 mol dm$^{-3}$ (M) was used, and 0.01 M BTA was added to the solution. After deaeration of the solution by bubbling of pure nitrogen gas, Py monomer was added by syringe at a 0.5 M concentration. The copper electrode was initially immersed in the solution for 600 s. After the immersion, electropolymerization of the PPy was started under constant current control at 2.0 mA cm$^{-2}$ in a 50 ml three-electrode cell. Platinum foil was used as the counter electrode. All potentials in the experiments here were measured with respect to a reference electrode of Ag/AgCl/ saturated KCl (SSE) with the potential of 0.197 V vs. SHE.

The mass change of the copper electrode during the PPy polymerization was monitored in situ by an electrochemical quartz crystal microbalance (EQCM), in which a frequency sensor, Maxtec KPS550, was coupled with a frequency counter, Advantest 5381. An Au coated AT-cut quartz crystal with a 5 MHz resonance frequency mounted in the frequency sensor was used as the working electrode. Before the PPy deposition, copper was electrodeposited on the Au coated quartz crystal in a solution containing 0.5 M H$_2$SO$_4$ and 0.5 M CuSO$_4$ at 24 mA cm$^{-2}$ for 360 s. About 2.8 mg cm$^{-2}$ of copper was deposited corresponding to a thickness of about 3 µm. The EQCM measurements were performed in a three-electrode cell with a volume of 250 cm$^3$. The mass change ($\Delta m$) was estimated from the frequency change by the Sauerbrey equation simplified to the following.

$$\Delta m = -K\Delta f$$ (5-1)
The value of $K$ was determined for the 5 MHz resonance frequency at $K = 28 \text{ ng cm}^{-2} \text{ Hz}^{-1}$.

All the experiments were carried out at room temperature, 25 ($\pm 2$)$^\circ\text{C}$, unless otherwise noted.

For the characterization of the PPy layer deposited on copper, infrared reflection absorption spectroscopy (IR-RAS), Raman spectroscopy (RS), scanning electron microscopy (SEM), confocal laser scanning microscopy (CLSM), and glow discharge optical emission spectroscopy (GD-OES) were used. For the IR-RAS, a JASCO FT-IR 4000 was used, which is equipped with a CMT detector and a grazing angle measurement accessory, JASCO RAS PO410-H, with an incidence angle of 85$^\circ$. Transmittance spectra were measured through KBr-pellets. For the RS, a Raman spectrometer (Bunko-Keiki M30-TP-M) was used, in which the excitation was produced by an YVO$_4$ solid-state laser beam at 532.0 nm wavelength and the detection of the scattered light was achieved with a highly sensitive CCD (Andor DO4041A). The excitation laser power was controlled below 5 mW to avoid damaging the PPy films.

The surface morphology of the PPy layer on the copper was observed using SEM, JEOL JSM-6510LA. The depth profile of the elements in the PPy films was measured by GD-OES, Horiba JY-5000 RF. The thickness and surface roughness of the PPy film were measured by CLSM, Laser-Tech 1LD21D. The thickness was evaluated by measuring the difference between the coated and uncoated copper surfaces. For the surface roughness, the arithmetic mean roughness ($R_a$) was calculated with the
following equation,

\[ R_a = \frac{\sum |Z_i - Z_{av}|}{N} \]  \hspace{1cm} (5-2)

where \( Z_i \) is the level at a site \( i \), \( Z_{av} \) the average level, and \( N \) is the number of sites measured. The adhesion strength of the PPy film to the copper substrate was measured by a sellotape test which consists in cutting the PPy film into small squares, sticking tape onto the squares and then stripping the tape from the squares. The ratio of the number of adhering film squares versus the total number was used as the adherence strength expressed in percentages.

The corrosion of the copper covered with the PPy film was examined during immersion at 25 (±1)°C in 3.5 wt.% NaCl solution in which the open circuit potential (OCP) of the copper covered by the PPy layer was monitored against SSE by a Hokuto-Denko HE-104 potentiometer and a Graphtec Midi Logger GL-450 data logger. The amount of copper ions dissolved in the NaCl solution was measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES; Thermo-ICAP 6000).

A linear sweep voltammogram was measured in the NaCl solution by a Hokuto Denko HZ-5000 potentiostat in a 100 ml glass cell.

5.3 Results

5.3.1 BTA adsorption on copper (BTA-ad-Cu)

When copper is immersed in a BTA-containing solution, a protective adsorption
layer is assumed to form and inhibit copper corrosion [22]. The formation of the BTA layer on copper during the initial 600 s immersion was examined by EQCM. Fig. 5-1 shows the mass changes of the copper electrodes during the initial 600 s in the solution of oxalic acid and Py monomer containing BTA (Ox-Py-BTA solution) and not containing BTA (Ox-Py solution). In Fig. 5-1, the mass of the copper electrode slowly decreased without BTA. With BTA, however, the mass gradually increased, by 1.5 µg cm⁻² after 600 s of immersion. The mass increase of the electrode is due to the adsorption of BTA and a Cu-BTA complex layer formation.

**Fig. 5-1** Mass changes of Cu during the initial 600 s of immersion in Ox-Py and Ox-Py-BTA solutions.

The adsorption of BTA on the copper electrode was confirmed with the IR-RAS spectra. Fig. 5-2 shows the IR-RAS spectrum (curve (a)) of the copper electrode immersed in the BTA-containing solution for 600 s. The transmission absorption spectrum (TAS) of the BTA diluted in KBr pellet is shown as curve (b). In Table 5-1, the transmission absorption peaks of BTA are listed with their corresponding IR-RAS peaks. The strong peak at 1209 cm⁻¹ on IR-TAS assigned to the breathing vibration of
the triazole ring in BTA [23] is shifted to 1157 cm\(^{-1}\) on IR-RAS. Chadwick et al. [24] also observed the shift in the position of the triazole ring vibration, and reported that the shift originated in a coordination of the Cu to the ring nitrogen. In addition, the low absorbance of N–H stretching at 3400–3300 cm\(^{-1}\) and absence of the N–H bending at 1580–1630 cm\(^{-1}\) with IR-RAS also indicate the BTA on copper is mainly deprotonated benzotriazole (BTA\(^{-1}\)). The IR-RAS spectrum indicates that BTA coordinates to the copper ions on the surface.

**Table 5-1** Assignment of IR-RAS and TAS bands for BTA adsorbed on copper and for BTA.

<table>
<thead>
<tr>
<th>Experimental wave number ((\nu/cm^{-1}))</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>TAS of Pure BTA</td>
<td>IR-RAS of BTA-ad-Cu</td>
</tr>
<tr>
<td>3400- 3200</td>
<td>3400- 3200(weak)</td>
</tr>
<tr>
<td>3078- 3032</td>
<td>3100- 3046</td>
</tr>
<tr>
<td>1630- 1580</td>
<td>–</td>
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<td>1517- 1460</td>
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<tr>
<td>1092</td>
<td>–</td>
</tr>
<tr>
<td>1026</td>
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</tr>
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<td>–</td>
</tr>
<tr>
<td>1007,741</td>
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</tbody>
</table>
**Fig. 5-2** Reflection IR-RAS spectrum of the Cu surface immersed in Ox-Py-BTA solution ((a), bottom) and IR transmission absorption spectrum of BTA ((b), top).

### 5.3.2 Electropolymerization

**Fig. 5-3** The potential ((a), _________) and mass changes ((b), _________) during PPy polymerization in the Ox-Py-BTA solution and the potential ((c), _________) and mass changes ((d), _________) in the Ox-Py solution.
For the effect of BTA on the PPy formation on copper, anodic electropolymerization by a constant current was performed in the oxalic solution with BTA (Ox-Py-BTA) and without BTA (Ox-Py). The potential and mass changes ($\Delta m$) of the copper electrode during the PPy polymerization are shown in Fig. 5-3. The lines (a) and (b) indicate the potential and mass changes, respectively, in the Ox-Py-BTA solution and lines (c) and (d) are for the potential and mass changes, respectively, in the Ox-Py solution. In the Ox-Py solution the potential transient during the polymerization was characterized by two stages. At the first stage the potential revealed a plateau at about 0.2 V. At the second stage the potential rose sharply to a peak value and then slowly decreased to a steady value. The mass changed in the different stages initially it decreased, and then increased steadily as shown by line (d) in Fig. 5-3. After the potential peak, the rate of the mass increase weakened and during the time of the second potential plateau at 0.6 V, the mass increase was linear. As reported elsewhere [13,25], the potential peak corresponds to the over-potential for nucleation of PPy and the following potential plateau to three dimensional growth of the PPy film.

In the Ox-Py-BTA solution, the potential initially increased without any initial plateau from the immersion potential of $-0.25$ V to a peak and then rapidly decreased to the second potential plateau. The mass increased linearly with time without any delay. The linear increase in the mass may indicate that the PPy film grows uniformly with the charge applied. The layer of the Cu-BTA complex on the copper surface formed during the initial 600 s immersion plays a large role in the uniform growth of
the PPy film on copper. In addition, both the peak and plateau potentials in the Ox-Py-BTA solution were lower than those in the Ox-Py solution.

![Graph and images](image)

**Fig. 5-4** Potential transients during the formation of PPy on copper in Ox-Py-BTA solution (A) and in Ox-Py solution (D), and SEM micrographs of the PPy film taken out at (C) 0.1 C cm\(^{-2}\) and (D) 0.6 C cm\(^{-2}\) in Ox-Py BTA solution and at (E) 0.2 C cm\(^{-2}\) and (F) 0.6 C cm\(^{-2}\) in Ox-Py solution. The PPy films were prepared at 2.0 mA cm\(^{-2}\) at charge of B, C in Fig. (A), and at E, F in Fig. (D), respectively.

For more details of the effect of BTA on the PPy deposition, the surface morphology of the PPy film formed in the Ox-Py-BTA and Ox-Py solution was observed by SEM. Fig. 5-4 shows SEM photographs taken at B, C, E, and F as indicated in Fig. 5-4(A) and (D). In the Ox-Py-BTA solution, a smooth and thin PPy layer is observed at B, a charge of 0.1 C cm\(^{-2}\) (Fig. 5-4(B)), and at C with the higher
charge, the PPy has grown to a thick uniform PPy film (Fig. 5-4(C)). In the Ox-Py solution, however, the PPy did not cover whole surface at E, at the polymerization charge of 0.2 C cm\(^{-2}\), and PPy clusters with different diameters were distributed across the surface (Fig. 5-4(E)). The PPy dark colored clusters in the SEM photograph by EDS showed strong nitrogen signals and less nitrogen was detected in the other areas. With continued growth, after the situation in Fig. 5-4(E), it is considered that, the PPy clusters continue growing laterally and combine with each other, finally to cover the whole of the substrate (Fig. 5-4(F)).

![Fig. 5-5 3-Dimesional view of the PPy film formed on copper (A) in the Ox-Py-BTA solution and (B) in the Ox-Py solution. The PPy films were prepared at 2.0 mA cm\(^{-2}\) for 500 s.](image)

For evaluating the surface unevenness of the PPy film formed, the surface of the film was observed by CLSM. Three dimensional views of the surface of the PPy films formed at 2 mA cm\(^{-2}\) after 500 s in the Ox-Py-BTA and Ox-Py solutions are shown in Figs. 5-5(A) and (B), respectively. From these three-dimensional views we estimated the mean roughness of the level on the PPy film surface (Ra), for the PPy film formed
in the Ox-Py-BTA solution $Ra = 0.4 \, \mu m$ and for the film in the Ox-Py solution $Ra = 0.8 \, \mu m$. The addition of BTA results in the formation of a more smooth PPy film.

The mass change during the constant current polymerization of the PPy film was measured by EQCM, as a function of charge passed. Fig. 5-6 shows the mass change as a function of the charge during the PPy polymerization in the Ox-Py-BTA (curve (b)) and in Ox-Py (curve (c)) solution, the mass change on a gold electrode is plotted as curve (a) in Fig. 5-6 allowing a comparison. On the gold electrode, the PPy film grows uniformly at a rate of $266 \, \mu g \, C^{-1}$ in Ox-Py, while for the PPy film formed in Ox-Py-BTA on copper, the mass initially shows a small plateau, then increases linearly with the charge, and the mass to charge ratio is very similar to that on gold. The mass of the PPy film formed on copper in Ox-Py (curve (c) in Fig. 5-6) is slightly smaller than that of PPy on Au, and this lower rate of growth may be due to anodic dissolution of copper during PPy electropolymerization. The thickness of PPy film formed on the copper in Ox-Py-BTA at $2.0 \, mA \, cm^{-2}$ after 500 s was measured by CLSM. The thickness was evaluated with the difference between the parts covered and not covered with PPy. The thickness of the PPy film thus evaluated was $1.3 \, \mu m$, and from the thickness and mass in Fig. 5-6, the average density of the PPy was evaluated to be $2.0 \, g \, cm^{-3}$.
Fig. 5-6 Mass gains of the electrodes as a function of the charge during PPy formation (a) on Au in Ox-Py solution, (b) on Cu in Ox-Py-BTA solution and (c) on Cu in Ox-Py solution.

To check the adhesion between the PPy film and the copper, a sellotape test was performed and the resulting surfaces are shown in Fig. 5-7. All parts of the PPy film formed in the Ox-Py-BTA solution remained on the copper surface after peeling with the cellotape (Fig. 5-7(A)). For the PPy film in the Ox-Py solution, however, all of the film was removed from the copper by the sellotape (Fig. 5-7(B)). This shows that the PPy film formed in the solution containing BTA is more adhesive.

Fig. 5-7 Photographology of the PPy films after the cellotape test. (A) PPy prepared...
on Cu in Ox-Py-BTA solution and (B) in Ox-Py solution. The PPy films were formed at 2.0 mA cm\(^{-2}\) for 1000 s.

5.3.3 Characterization of the PPy film deposited on the BTA-pretreated copper

The depth profile of the PPy film formed on the copper in the Ox-Py-BTA solution was measured with GD-OES and the results are shown in Fig. 5-8. The depth profile indicates the presence of the N, C, and O elements which correspond to those in the polymer and the doped counter ions. Three regions may be distinguished in the depth profile: an outermost region which can be attributed to the PPy layer doped with oxalate, an intermediate region associated with a thin BTA-Cu complex layer, and the inner region related to the copper substrate.

![Depth profile of the PPy film](image)

**Fig. 5-8** Depth profiles of the PPy formed on Cu in Ox-Py-BTA solution. The PPy film was formed at 2.0 mA cm\(^{-2}\) for 500 s.
Fig. 5-9 (A) IR-RAS spectra of the PPy films formed on Cu in the Ox-Py-BTA and in the Ox-Py solution, (B) Raman spectra of the PPy film formed on Cu in the Ox-Py-BTA and in the Ox-Py solution.

During the polymerization in the solution containing BTA, BTA was assumed to be doped into the PPy film in addition to doping of oxalate. To confirm the doping of BTA, the IR-RAS and RS of the PPy formed in the solution containing BTA or not were measured. Fig. 5-9(A) shows the IR-RAS spectra of the PPy films formed in the Ox-Py-BTA and Ox-Py solution and Fig. 5-9(B) shows the RS spectra of the PPy films formed in the two solutions. The IR absorption peaks of the PPy film has been reported in other studies [12,26-29]. The peaks in Fig. 5-9(A) were assigned to absorption of the PPy and oxalate doped, and details of the assignment are listed in Table 5-2. From a comparison of the absorption peaks of the PPy layer in Fig. 5-9 with those of the BTA in Fig. 5-2, the weak absorbance peaks at 1201 and 741 cm\(^{-1}\) can reasonably be assigned to the breathing vibration of the triazole ring of BTA and –C–H deformation in the aromatic ring of BTA. The presence of BTA in the PPy film was further proved by the RS in Fig. 5-9(B). Assignment details of the Raman
shift in Fig. 5-9(B) are given in Table 5-3, and the peak at 1180 cm⁻¹ may be seen to originate from the triazole ring stretching in BTA. Taken together, both the IR-RAS and RS results indicate the presence of BTA in the PPy film.

**Table 5-2** Assignment of IR-RAS bands for PPy-Ox-BTA and for PPy-Ox.

<table>
<thead>
<tr>
<th>Experimental wave number (ν/cm⁻¹)</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPy-Ox-BTA</td>
<td>PPy-Ox</td>
</tr>
<tr>
<td>1802</td>
<td>1802</td>
</tr>
<tr>
<td>1711-1657</td>
<td>1711-1657</td>
</tr>
<tr>
<td>1562-1459</td>
<td>1562-1459</td>
</tr>
<tr>
<td>1421</td>
<td>--</td>
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<tr>
<td>1297</td>
<td>1289</td>
</tr>
<tr>
<td>1201</td>
<td>--</td>
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<tr>
<td>1072</td>
<td>1120</td>
</tr>
<tr>
<td>1005</td>
<td>1033</td>
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<tr>
<td>913,791</td>
<td>913,776</td>
</tr>
<tr>
<td>741</td>
<td>--</td>
</tr>
</tbody>
</table>

**Table 5-3** Raman shifts and assignment of Raman bands for PPy-Ox-BTA layer and for the PPy-Ox layer.

<table>
<thead>
<tr>
<th>Experimental Raman shift(Δν/cm⁻¹)</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPy-Ox-BTA</td>
<td>PPy-Ox</td>
</tr>
<tr>
<td>1570</td>
<td>1580</td>
</tr>
<tr>
<td>1404</td>
<td>1401</td>
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<tr>
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<td>984</td>
<td>984</td>
</tr>
<tr>
<td>928, 871</td>
<td>928, 871</td>
</tr>
</tbody>
</table>

**5.3.4 Corrosion protection of copper by the PPy layer**

The effect of the BTA addition to the PPy film on the corrosion protection of
copper was evaluated by immersion in 3.5 wt.% NaCl solution, with the open circuit potential (OCP) monitored as a function of the immersion time and the amount of Cu ions dissolved in the NaCl solution measured by ICP-AES.

**Fig. 5-10** Change in OCP of the PPy-covered Cu with immersion time in 3.5 % NaCl aqueous solution. (a) The PPy film was prepared on Cu in Ox-Py-BTA solution, (b) in Ox-Py solution, and (c) bare copper. The PPy films were formed at 2.0 mA cm\(^{-2}\) for 500 s.

Fig. 5-10 shows the OCP change for the copper covered with the PPy (PPy-Ox-BTA) film formed in the Ox-Py-BTA solution. The OCP of the bare copper and the copper covered with the PPy-Ox film formed in the Ox-Py solution are also plotted here. The bare copper was kept at a relatively low potential of about −0.2 V and after 200 h of immersion it remained at an almost steady potential between −0.17 and −0.19 V. The coating of the PPy film shifted the OCP to the higher value. For the copper covered with the PPy-Ox layer, the OCP initially reached 0.15 V but within 6 h of immersion decreased to about −0.09 V. After immersion for 200 h the OCP...
reached about \(-0.12\) V and then maintained this potential. For the copper covered by the PPy-Ox-BTA film, there was a small decrease early in the immersion, and the OCP then increased to about 0.2 V that was maintained to 480 h of immersion time.

After 480 h of immersion, the average dissolution rate was estimated from the amount of copper ions dissolved was determined by ICP-AES. The rates of dissolution for the copper covered by PPy-Ox-BTA, the copper covered by PPy-Ox, and the bare copper were 0.37, 0.92, and 1.9 µg cm\(^{-2}\) h\(^{-1}\), respectively. From this the protective efficiency (\(PE\)) can be calculated as 80%, 51% for the PPy-Ox-BTA and PPy-Ox films as per the following equation.

\[
PE \% = \frac{v_0 - v_s}{v_0} \times 100\% \quad (5-3)
\]

with the \(v_0\) and \(v_s\) are the average dissolution rates of the bare copper and the copper covered by the PPy.

**Fig. 5-11** Potential-current curves (a) for the BTA-pretreated copper covered with PPy film, (b) copper covered with PPy film, and (c) bare copper in 3.5 % NaCl solution under air-opened conditions. The curve was measured by the potential sweep from
$E_{ocp} - 0.12 \text{ V to } E_{ocp} + 0.3 \text{ V at a sweep rate of } 2 \text{ mV s}^{-1}$.

To examine the protection mechanism, the potential-current curves for the bare copper and the copper covered by the PPy film were measured by linear potential sweep at a sweep rate of 2 mV s\(^{-1}\) in 3.5% NaCl solution under an air-opened condition after the copper electrodes had been immersed for 1 h. The potential range for the measurements was between $(E_{ocp} - 0.12) \text{ V and } (E_{ocp} + 0.3) \text{ V}$. The results are shown in Fig. 5-11, where the zero-current potential is seen to shift to higher potentials by the cover of the PPy film. The larger shift was seen for the PPy-Ox-BTA covered copper. The exchange current densities estimated from an extrapolation of the Tafel lines were 1-2 $\mu$A cm\(^{-2}\). The exchange current density of the bare copper corresponds to its corrosion current and, however, for the PPy-covered copper, they represent the following redox property of the PPy on copper.

$$\text{PPy}^{x+y}(x/y)A_{aq}^{y-} + ye^{-} \leftrightarrow \text{PPy}^{(x-y)x}(x-y)A^{y-} + A^{y-}_{aq} \quad (5-4)$$

where $A_{aq}^{-}$ represents the doped anion. When we notice the anodic branch in the plot, the current of the bare copper increase sharply to 100 $\mu$A cm\(^{-2}\) at $-0.16 \text{ V}$ and there is no passive region. Probably the pitting corrosion was generated at the relatively low potential. By the PPy film covering of copper, the anodic current is strongly suppressed and with the addition of BTA the suppression is further enhanced.

5.3.5 Self-healing of damaged site

When considering practical use of the conducting-polymer coatings for corrosion
protection of metallic components, the coating should possess self-healing properties with damaged sites spontaneously repaired and the corrosion at the site prevented or stopped.

Fig. 5-12 Changes in OCP of Cu covered by with PPy-Ox-BTA and PPy-Ox films during the immersion in 3.5 \% NaCl aqueous solution. The defect was created in the film after 24 h immersion. The PPy films were prepared at 2.0 mA cm\(^{-2}\) for 500 s.

Fig. 5-12 shows the potential change of copper covered by the PPy-Ox-BTA and PPy-Ox films during immersion in the NaCl solution. In Fig.12, The PPy-covered copper was initially immersed for 24 h, then removed from the solution. An artificial defect with an area of 5 mm × 0.2 mm was made by a knife on the PPy layers, and then the PPy-covered copper was again immersed in the solution for 120 h. For the copper covered by the PPy-Ox-BTA film, the OCP decreased from 0.1 to –0.08 V after introducing the defect and then the OCP slowly increased to –0.02 V during the following immersion. For the copper covered by the PPy-Ox film the OCP decreased from –0.05 to –0.08 V with the defect and then shifted further in the negative
direction. Photographs of the PPy-covered copper after the 120 h immersion in the NaCl solution are shown in Fig. 5-13. Large amounts of green corrosion products are observed around the scratch site on the copper covered by the PPy-Ox without BTA. There are corrosion products around the defect region on the copper covered by PPy-Ox-BTA, however the amount of the corrosion products is much smaller than that on the copper covered by PPy-Ox without BTA.

![Photographs of PPy-covered Cu with the artificial defect after 120 h immersion. (A) Cu covered by PPy-Ox-BTA and (B) Cu covered by PPy-Ox. The PPy films were prepared at 2.0 mA cm\(^{-2}\) for 500 s.](image)

**Fig. 5-13** Photographs of PPy-covered Cu with the artificial defect after 120 h immersion. (A) Cu covered by PPy-Ox-BTA and (B) Cu covered by PPy-Ox. The PPy films were prepared at 2.0 mA cm\(^{-2}\) for 500 s.

### 5.4 Discussions

#### 5.4.1 Effect of BTA addition on formation of PPy film

The formation of PPy on metal substrates from oxalate solutions has been extensively investigated [8,30,31]. With oxalate solutions, the formation of a stable PPy layer has been reported, likely due to an initial formation of a metal-oxalate salt layer which passivated the metal surface and facilitated the subsequent
polymerization-deposition of PPy. The EQCM measurements in Figs. 5-3 and 6 provide useful results to help understand the formation process of PPy in the Ox-Py solution employed here. As shown in curve (d) in Fig. 5-3 and curve (c) in Fig. 5-6, the specimen mass initially decreased and then sharply increased at the initial potential plateau. The initial decrease of the mass indicates a dissolution of copper, and the subsequent increase may be related to deposition of copper oxalate salt. With the dissolution of copper, accumulation of Cu ions takes place to induce precipitation of the salt layer. The copper oxalate salt layer is assumed to act as a passive film and inhibit further copper dissolution. On the salt layer the electropolymerization takes place, and the mass increases linearly with the growth of the PPy film.

When copper is immersed in the BTA containing solution, there is no initial potential plateau in Fig. 5-3 (curve b), and a relatively homogenous PPy film was observed after polymerization (Fig. 5-4(C) and Fig. 5-5(A)). A protective BTA layer or Cu ion-BTA complex layer was assumed to be formed on the copper during the initial immersion and this would inhibit dissolution of copper. The polymerization of PPy starts on this protective layer immediately after the anodic current is imposed. This suggestion is confirmed on the mass-time or mass-charge relations in Figs. 5-3 and 5-6.

It needs to note that both the peak and plateau potentials (curve (c) in Fig. 5-3) in the Ox-Py solution were higher than those in Ox-Py-BTA solution (curve (a) in Fig. 5-3). Full details of the reason for the potential increase are not fully understood, but it may be related to the dissolution of substrate and salt precipitation during the PPy
electropolymerization.

5.4.2 Effect of BTA addition on corrosion protection of PPy film

With a PPy film prepared on copper in an oxalic acid solution containing BTA, the following improvements in corrosion resistance were observed.

(1) The surface of the PPy film was more homogeneous than without BTA.

(2) Adhesion between the copper and the PPy film was stronger.

(3) Corrosion protection in NaCl solution was enhanced.

(4) The corrosion from flaws in the PPy film was suppressed.

The homogeneous PPy film is assumed to be caused by the BTA layer formed in the initial immersion. On the BTA layer, the Py monomers are easily coordinated and a large number of PPy nuclei are generated. The subsequent growth from the large number of PPy nuclei enables the formation of a relatively homogeneous film. For the absorption of BTA, coordination of the triazole ring to copper is expected, resulting in the strong adhesion between BTA and copper. Since the BTA absorbed layer may include coordinated Cu ions [32], the Py ring in the PPy layer is assumed to be strongly coordinated on the copper ions. These ideas might explain the strong adhesion between the copper substrate and the PPy layer.

High corrosion protection may be related to inclusion of BTA in the PPy film (Figs. 5-8 and 5-9) in addition to the effect of the homogeneous surface morphology and the strong adhesion. Synergistic effects of the oxidative property of the PPy film and the inhibitive property of BTA may further be suggested to enhance the ability of the
corrosion protection. The oxidative property of the PPy enables the copper to maintain the high potentials at which copper can be stably maintained in the passive state. When the PPy layer was damaged locally, the BTA included in the film may inhibit the corrosion progress from the damage sites. The inhibition of corrosion from an artificial flaw on the PPy-Ox-BTA film was shown in Figs. 5-11 and 5-12.

5.5 Conclusions

The following conclusions were drawn from the present investigation on the PPy film formed in oxalic acid solution containing BTA.

(1) A homogenous PPy film was anodically formed on a copper electrode by constant current control in an oxalic acid aqueous solution containing Py monomer and BTA.

(2) The addition of BTA to the oxalic acid solution facilitated both the formation of the PPy film on the copper substrate as well as it promoted the adhesive strength of the PPy film on the copper.

(3) The PPy film prepared in the oxalic acid solution containing BTA protected copper against corrosion in 3.5 wt.% NaCl solution for a longer time period. After 480 h of immersion, copper dissolution was inhibited with 80% protection efficiency relative to that with bare copper. The protective property may be assumed to be caused by the presence of BTA on the copper surface and in the PPy film.

5.6 References

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Chapter VI

Summary

In chapter I, previous studies of conducting polymers (CPs) were reviewed, in which the origin of conductivity, doping of ions into CPs, synthesis method, mechanism of electropolymerization of conducting polypyrrole (PPy) were introduced. The previous studies on the protection of copper against corrosion by CP film were summarized. The present issues on the corrosion protection of copper and its alloys were surveyed and the aim of this work was described.

When one uses copper at seashore or in seawater, surface finishing for enhancement of corrosion resistivity of copper is required. In this study, the new anti-corrosion technique has been developed by a conducting polymer (CP) coating using polypyrrole (PPy) film. For the stable anti-corrosive surface finishing, a self-healing property should be incorporated in the surface coating. For the self-healing property, the PPy film has been doped with corrosion inhibitors of copper, for which Phytic acid ($C_6H_{18}O_{24}P_6$, IP$_6$) and benzotriazole (BTA) have been adopted in this study.

In chapter II, a PPy doped with phytic acid ($C_6H_{18}O_{24}P_6$, IP$_6$) ions was electrosynthesised on copper from an aqueous phytic acid solution. The phytic acid ($C_6H_{18}O_{24}P_6$), which works as the principal phosphorous storage in many plant tissues,
is considered as one of the green materials. The growth of the PPy film at the copper surface was facilitated by formation of a copper-phytate pseudo-passive layer formed in the initial oxidation of the copper electrode in the phytic acid solution. This layer inhibited dissolution of copper and allowed electropolymerization of the pyrrole on the surface. The protection of copper by the PPy film was tested in 3.5 wt% NaCl aqueous solution. The open circuit potential (OCP) of the copper covered with the PPy-IP$_6$ in the NaCl solution was maintained in a high potential state for the period longer than 800 h and the dissolution of copper covered with PPy-IP$_6$ was decreased to 1/19 relative to that of bare copper.

In chapter III, we discussed the effects of the solution pH and applied CD on the PPy polymerization-deposition process on copper electrode as well as on the protection property of the PPy film. The oxidation degree of the PPy film depended on the solution pH for preparation, increasing with the more acidic solution. In the more acidic solution, the higher CD is required to form the PPy layer. When one oxidized bare copper in phytic acid solution at various pHs containing pyrrole monomer, a thin layer consisting of complex compound of Cu-IP$_6$ was firstly formed, followed by the formation of the PPy layer doped with IP$_6$ on the complex compound layer. The complex compound layer passivated the copper surface and its thickness increased with the lower pH value of the solution and the lower CD applied. Protective property of the PPy films also depended on the solution pH. It was found that the PPy coating prepared in the IP$_6$ solution at pH 4 exhibited the most protective property against copper corrosion.
In chapter IV, two different PPy coatings were coated on copper from phytic acid and sodium di-hydrogen phosphate solution. The corrosion protection of copper by the PPy coatings were investigated in 3.5 % NaCl, by electrochemical quartz crystal microbalance (EQCM) and electrochemical impedance spectroscopy (EIS). The PPy film doped with Phy$^{6-}$ anions (PPy-Phy$^{6-}$) was found to work as a cationic perm-selective membrane and to effectively inhibit penetration of chloride ions to the PPy film. The copper covered with PPy-Phy$^{6-}$ was thus maintained in passive state for the longer period than 2 months and the dissolution of the copper were inhibited by 1/100 relative to that of bare copper. The copper covered with PPy-H$_2$PO$_4^-$ film prepared in sodium di-hydrogen phosphate solution possessed an anionic perm-selectivity and the dissolution of copper was inhibited by 1/13. The degradation of the PPy films was examined by EIS and EQCM during the immersion in the NaCl solution. It was observed that the impedance of the PPy film doped with H$_2$PO$_4^-$ decreased during the immersion, while the impedance of PPy film doped with phytate anions increased.

In chapter V, benzotriazole (BTA) was added to the solution for Polypyrrole (PPy) deposition in oxalic acid solution. A homogenous PPy film was anodically formed on a copper electrode by constant current control in an oxalic acid aqueous solution containing Py monomer and BTA. Effect of the BTA addition on the PPy formation and on its corrosion property was investigated with different methods by comparing to
the control samples. The addition of BTA to the oxalic acid solution facilitated the formation of the PPy film on the copper substrate and enhanced the adhesive strength of the PPy film on the copper. The PPy film prepared in the oxalic acid solution containing BTA (PPy-Ox-BTA film) effectively protected copper against corrosion in 3.5 wt. % NaCl solution. After 400 h immersion, dissolution of copper covered with PPy-Ox-BTA was decreased to 20% relative to that of bare copper. The protective property may be assumed to be caused by the presence of BTA on the copper surface and in the PPy film.

In chapter VI, the summary of the thesis was described.
List of papers


(4) Y. H. Lei, T. Ohtsuka, A. Hyono, M. Ueda, Electrochemical impedance spectroscopy and electrochemical quartz crystal microbalance to study the corrosion process of PPy-coated copper in aqueous solution, *Corrosion Science*, 2014 (under review)


List of Presentations


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