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The effect of ultrasonic irradiation during
electropolymerization of polypyrrole on corrosion
prevention of the coated steel

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1. Abstract

Ultrasonic irradiation was imposed during electropolymerization of polypyrrole (PPy) in acid phosphate solution containing molybdophosphate ($\text{PMo}_{12}\text{O}_{40}^{3-}$) ions and pyrrole monomer. Corrosion of the steel coated by the PPy film prepared under ultrasonic irradiation was tested in 3.5 wt.% NaCl solution and compared with corrosion of the steel coated by the PPy film without ultrasonic irradiation. The PPy film prepared under ultrasonic irradiation kept the steel in the passive state one and a half times as long as that prepared without ultrasonic irradiation. Imposition of ultrasound enhanced the doping of $\text{PMo}_{12}\text{O}_{40}^{3-}$ and decreased the doping of HPO_4^{2-} . The surface morphology of the PPy film was changed with imposition of ultrasound in electropolymerization process. Under imposition of ultrasound, a dense and compact PPy layer was formed. The structure of the PPy film obtained under ultrasonic irradiation was assumed to result from change in nucleation-growth mechanism.

Keywords: A. Polypyrrole; A. Conductive polymer; B. GD-OES; C. Corrosion protection; C. Ultrasonic irradiation

2. Introduction

In the last decades, conductive polymers (CPs) such as polyaniline, polypyrrole, and their derivatives have been widely investigated as corrosion-resistant coatings [1-9]. From environmental aspect, CP coatings have been considered as a substitute for chromate treatment because their oxidative and catalytic properties induce the stable passive state of steels [1,3]. In our previous work, we investigated PPy films doped with Keggin structure ions of $\text{PMo}_{12}\text{O}_{40}^{3-}$ for corrosion prevention of steel [10]. Further improvement of the corrosion resistance was achieved by introduction of over-layer doped with large size organic counter anions [11,12]. The corrosion resistance was found to depend on electronic and structural properties of oxidized PPy films.

Ultrasonic irradiation has recently been applied to chemical [13 - 15] and electrochemical [16-18] synthesis of CPs. It has been reported that structural properties of polymer films can be modified by ultrasound imposed during polymerization process.

It is well known that the imposition of ultrasound in a liquid medium allows to generate cavitation bubbles, which grow and collapse, greatly changing the pressure and temperature inside the bubble [19,20]. Due to the high temperature, many kinds of chemical reactions take place inside bubble as well as vaporization. For example, OH radicals and accompanied other oxidants can be created at the cavitation bubbles and dispersed in liquid solution to induce various reactions [21]. The above phenomena may change the synthesis or electrosynthesis conditions for the CP preparation to modify the structure of the CP films.

The aim of this study is to investigate the effects of ultrasonic irradiation on electropolymerization of PPy occluding a Keggin structure ions of $\text{PMo}_{12}\text{O}_{40}^{3-}$ on steel. The PPy layer prepared under ultrasonic irradiation revealed better corrosion resistance than that without irradiation.

3. Experimental

Pyrrole monomer (Py) purchased from Kanto Chemical Co. (99% purity) was used without any pretreatment. All the other reagents at analytical grade were purchased from Wako Pure Chemical Ltd. Solutions used were prepared from double distilled and subsequently deionized Milli-Q water, and deoxygenated by nitrogen bubbling for 30 min before use. The carbon steel with the composition of C 0.032, Si 0.013, Mn 0.15, P 0.012, S 0.008, Al 0.018 and Fe 99.767 wt. % was mechanically polished with 800-grade abrasive paper and degreased in acetone in ultrasonic bath before use. The geometrical surface of the steel electrodes was about 3 cm².

A three-electrode cell with 50 cm³ volume was used for electrodeposition of PPy on the steel substrate. A Ag/AgCl/sat. KCl and a platinum foil were used as reference and counter electrodes, respectively. Ultrasonic generator employed was a NISSEI US-50 model equipped with a tip 5 mm in diameter emitting 28 kHz sound with 50 W. The electrodeposition was carried out at room temperature of about 25 °C. The imposition of ultrasound, however, increased the temperature of the electrolyte in the cell to 44 °C after 30 min.

Electrosynthesis process was preceded by passivation of steel in 0.06 M disodium molybdate (Na₂MoO₄) solution under potentiostatic condition at 0.8 V for 30 min. After that, the solution was exchanged with solution containing 0.2 M H₃PO₄, 5 mM H₃PMo₁₂O₄₀ (H₃PMo₁₂), and 0.1 M pyrrole (Py) monomer. PPy was formed galvanostatically at a constant current of 1.0 mA cm⁻².

Thicknesses of the PPy films were measured by the Confocal Laser Scanning Microscopy "Laser-Tech 1LD21D". Evaluation of the thickness was done by measuring the distance difference between coated and uncoated steel surfaces.

Depth profile of elements in the PPy films was measured by the Glow Discharge Optical Emission Microscopy (GD-OES) "JY-5000 RF" with sampling diameter of 5mm.

The corrosion tests of the PPy coated steel were carried out at 25.0 ± 0.3 °C in the 3.5 wt.% NaCl solution in which the open circuit potential (OCP) was continuously recorded for 4 days.

4. Results

4.1 Electropolymerization of pyrrole on steel substrate

The electrodeposition of polymer can be achieved on inert electrodes like platinum (Pt) or gold (Au). Less noble metals like iron (Fe) or zinc (Zn) undergo dissolution during anodic polarization in the most aqueous solution used, and thus polymer film cannot be formed directly on the metal substrate. Formation of the oxide film on the metal substrate at a constant potential of 0.80 V vs. Ag/AgCl/sat. KCl in Na_2MoO_4 aqueous solution preceded the synthesis of the polymer. The electropolymerization of PPy film was performed at a constant current density of 1.0 mA cm^{-2} with and without imposition of ultrasonic irradiation after the formation of the thin oxide film. Figure 1 shows the mass change of the PPy film formed by galvanostatic electrodeposition as a function of charge passed. The relationship between the film mass and electric charge passed is linear with regression coefficients at 0.998 and 0.994 for polymerization without and with imposition of ultrasound in electropolymerization medium, respectively. As seen in Fig. 1, a significant increase of the ratio of $\Delta m/\Delta Q$ is observed on the polymerization under ultrasonic irradiation.

The thicknesses of the PPy films were evaluated by confocal laser scanning microscopy (CLSM). Table 1 shows the ratio of thickness to electricity passed during polymerization and density (the ratio of mass to thickness) of the PPy films. As seen in

Table 1, the PPy film prepared under ultrasonic irradiation possesses a higher density of 3.9 g/cm^3 than that prepared without ultrasonic irradiation.

The FE-SEM micrographs of PPy films galvanostatically electrodeposited with electricity from 0.5 to 2 C cm^{-2} are shown in Fig. 2. The PPy films show globular morphology and the particles size depends on the preparation method and the electropolymerization charge, growing with charge passed during the polymerization. In the electropolymerization without ultrasonic irradiation the particles range in size from 0.5 to 3 , from 0.5 to 4 , and from 0.5 to $6 \text{ }\mu\text{m}$ for the charge of 0.5 , 1.5 , and 2.0 C cm^{-2} , respectively. For polymerization under ultrasonic irradiation, particles in size from 0.5 to 2 , and from 0.5 to $3.5 \text{ }\mu\text{m}$ are observed for PPy electrodeposited with electricity of 0.5 , and 1.0 C cm^{-2} , respectively, and further increase of the polymerization charge does not significantly change the morphology of PPy film. From the particle size, it is seen that the PPy film consists of the finer particles under ultrasonic irradiation. It is thus suggested that the imposition of ultrasound produces denser and smoother PPy films.

4.2 Depth profile of the PPy films

PPy films galvanostatically electrodeposited on carbon steel with electricity of 1.0 C cm^{-2} were analyzed by Glow Discharge – Optical Emission Spectroscopy (GD-OES). The depth profiles of PPy films electrodeposited without and with ultrasonic irradiation are shown in Figs. 3 and 4, respectively. The profiles reveals signals of C and N, corresponding to the polymer matrix, and signals of P, Mo and O corresponding to the doping anions of $\text{PMo}_{12}\text{O}_{40}^{3-}$ and HPO_4^{2-} . The shorter sputtering time to the steel

substrate was observed for PPy film prepared without ultrasonic irradiation. It is in agreement with the lower thickness evaluated by CLSM. The intensity ratio of C and N is different between films prepared with and without ultrasonic irradiation during the PPy electropolymerization. When one considers an ordinary PPy matrix, the intensity ratios of N/C might be the same, being independent of the polymerization procedure. The difference in the signal intensity ratio may indicate some structural change, although, we could not explain the difference in the intensity ratio. The intensity ratio of Mo to P also is different between films prepared with and without ultrasonic irradiation. The difference indicates that the doping concentration of $\text{PMo}_{12}\text{O}_{40}^{3-}$ and HPO_4^{2-} anions changes with ultrasonic irradiation during the PPy polymerization.

4.3 Corrosion tests

The corrosion tests were performed in 3.5 wt.% NaCl aqueous solution where open circuit potential (OCP) as a function of time was recorded. For the test, the steels were covered by the PPy film galvanostatically prepared by the same electricity at 2.0 C cm^{-2} . Fig. 5 shows the OCP for the steels coated by PPy films prepared with and without ultrasonic irradiation. The steel covered by PPy film prepared without ultrasonic irradiation initially exhibits potential at 0.22 V and gradually decrease to stable potential at around 0.15 V after 6 h immersion. The relatively high potential indicates that the steel is kept in the passive state by oxidized PPy film. The potential is kept for 32 h in which no appreciable corrosion takes place. Potential rapidly decreases to around -0.3 V after 32 h immersion and gradually decrease to active potential of steel.

For the steel coated by the PPy film electrodeposited under ultrasonic irradiation the first decrease of the potential is not observed. The potential at 0.15 V in the passive range is kept for 46 h immersion. The PPy film prepared under ultrasonic irradiation kept the steel in the passive state by 14 h longer than PPy film prepared without ultrasonic irradiation.

5. Discussion

5.1 The effect of ultrasonic irradiation on composition of PPy film

It was found from Figs. 3 and 4 that the composition of the PPy film electrodeposited under ultrasonic irradiation was different from that without ultrasonic irradiation.

The electropolymerization process can be expressed by following reaction:

where, n is the number of moles of pyrrole monomer, y_1 and y_2 are the doping levels of molybdophosphate and phosphate anions, respectively [22,23]. The value of x is a valency of oxidized PPy per Py unit, i.e., $1/x$ represents the number of pyrrole units per one positive charge. If we assume that i) the current efficiency for electropolymerization of Py is 100%, ii) there is no water penetration into the PPy film, and iii) only $\text{PMo}_{12}\text{O}_{40}^{3-}$ and HPO_4^{2-} ions are doped into PPy matrix, the mass change on the electrode can be expressed by the Faraday law according to reaction (1):

$$\frac{\Delta m}{\Delta Q} = \frac{M_{\text{Py}} + y_1 M_{\text{PMo}_{12}\text{O}_{40}^{3-}} + y_2 M_{\text{HPO}_4^{2-}}}{(2 + 3y_1 + 2y_2)F} \quad (2)$$

where, M_{Py} , $M_{\text{PMo}_{12}\text{O}_{40}^{3-}}$, and $M_{\text{HPO}_4^{2-}}$ are the molar masses of the Py unit, the $\text{PMo}_{12}\text{O}_{40}^{3-}$ dopant, and the HPO_4^{2-} dopant, respectively ($M_{\text{Py}}=65 \text{ g mol}^{-1}$, $M_{\text{PMo}_{12}\text{O}_{40}^{3-}}=1834 \text{ g mol}^{-1}$, and $M_{\text{HPO}_4^{2-}}=95 \text{ g mol}^{-1}$). F is the Faraday's constant and $(2 + 3y_1 + 2y_2)$ represents the

number of electrons required for the oxidation of Py monomer for polymerization and the following doping process to the polymer. In the previous paper we reported $y_2=2.2y_1$ by the GD-OES measurements for the PPy film galvanostatically prepared without ultrasonic irradiation. From $y_2=2.2y_1$, the doping level of $\text{PMo}_{12}\text{O}_{40}^{3-}$ ions can be described in equation (3).

$$y_1 = \frac{M_{Py} - 2 \frac{\Delta m}{\Delta Q} F}{7.4 \frac{\Delta m}{\Delta Q} F - M_{\text{PMo}_{12}\text{O}_{40}^{3-}} - 2.2 M_{\text{HPO}_4^{2-}}} \quad (3)$$

Figure 6 shows the intensity ratio of P/Mo in the GD-OES measurements as a function of sputtering time for the PPy films prepared under ultrasonic irradiation and without ultrasonic irradiation. From Fig. 6 it is seen that the concentration of phosphorus for the film prepared under ultrasonic irradiation is about a third as high as that for the film prepared without ultrasonic irradiation. When the same calibration adopted in the previous paper [11] was applied to the intensity ratio, phosphorus in the film prepared under ultrasonic irradiation was estimated to be originated only in $\text{PMo}_{12}\text{O}_{40}^{3-}$. This means that the doping counter ions in the PPy film formed under ultrasonic irradiation are mainly $\text{PMo}_{12}\text{O}_{40}^{3-}$ ions and concentration of HPO_4^{2-} in the PPy film is extremely low. From Fig. 6, it is seen that the small amount of HPO_4^{2-} is present in the inner part of the film.

If we assume $y_2=0$ for the PPy film prepared under ultrasonic irradiation the value of y_1 can be calculated in Eq. (4) as a function of $\Delta m/\Delta Q$ which is the slope in Fig. 1.

$$y_1 = \frac{M_{Py} - 2 \frac{\Delta m}{\Delta Q} F}{3 \frac{\Delta m}{\Delta Q} F - M_{\text{PMo}_{12}\text{O}_{40}^{3-}}} \quad (4)$$

The doping level of $\text{PMo}_{12}\text{O}_{40}^{3-}$ as well as that of HPO_4^{2-} thus calculated is listed in Table 2. The doping levels of $\text{PMo}_{12}\text{O}_{40}^{3-}$ ions and HPO_4^{2-} ions for the PPy film electrodeposited without ultrasonic irradiation are 0.044 and 0.097, respectively. These values mean that one $\text{PMo}_{12}\text{O}_{40}^{3-}$ ion and one HPO_4^{2-} ion are doped for every 23 Py units and 10 Py units, respectively. When the ultrasound is imposed in electropolymerization of Py, the doping level of $\text{PMo}_{12}\text{O}_{40}^{3-}$ is about double and no HPO_4^{2-} ions are doped.

The difference in the doping between under ultrasonic irradiation and without ultrasonic irradiation may be explained by an aggressive agitation due to the irradiation. Although the concentration of $\text{PMo}_{12}\text{O}_{40}^{3-}$ ions in the solution is one-fortieth of that of HPO_4^{2-} ions, comparable doping of $\text{PMo}_{12}\text{O}_{40}^{3-}$ ions to the doping of HPO_4^{2-} ions takes place in the PPy film prepared without ultrasonic irradiation. This means that the doping of $\text{PMo}_{12}\text{O}_{40}^{3-}$ ions is induced more preferentially than that of HPO_4^{2-} ions. From the low concentration of $\text{PMo}_{12}\text{O}_{40}^{3-}$ ions, we can assume that the doping process of $\text{PMo}_{12}\text{O}_{40}^{3-}$ is determined by diffusion control. Under ultrasonic irradiation, the aggressive agitation takes place in the electrolyte and the diffusion of ions is greatly accelerated. The enhanced diffusion of $\text{PMo}_{12}\text{O}_{40}^{3-}$ to the steel surface may bring about further acceleration of the preferential doping of $\text{PMo}_{12}\text{O}_{40}^{3-}$.

5.2 The effect of ultrasonic irradiation on morphology of PPy film

The change in morphology of the PPy films electrodeposited under ultrasonic irradiation is supposed to result from change of mechanism of nucleation and growth of the polymer film [24-29].

The ultrasonic irradiation may give physical effect like cavitation to the substrate surface and the solution. Such effect may enhance the rate of nucleation of PPy deposition. The number of nuclei generated in the initial stage of polymerization will be higher under the ultrasonic irradiation than that without the irradiation. The larger number of nuclei may produce globules with relatively small size and a relatively flat surface. Without the ultrasonic irradiation, large size globules can grow from the smaller number of nuclei and the surface may be more rough.

5.3 Corrosion prevention of steel by PPy coatings

From Fig. 5, it was found that the PPy film electrodeposited under ultrasonic irradiation exhibited better corrosion performance for steel.

The protection of the coating may result from formation of the stable passive oxide film at the metal-polymer interface due to oxidative action of PPy and passivator action of $\text{PMo}_{12}\text{O}_{40}^{3-}$ [12]. As seen in Table 2 the oxidized state of the PPy film prepared under ultrasonic irradiation was comparable to that of PPy prepared without ultrasonic irradiation. The doping level of $\text{PMo}_{12}\text{O}_{40}^{3-}$ ions was twice higher for the PPy film prepared under ultrasonic irradiation. Since the $\text{PMo}_{12}\text{O}_{40}^{3-}$ ions act as a strong passivator, the PPy film prepared under ultrasonic irradiation may stabilize the passive oxide film for longer period of time. The PPy film prepared under ultrasonic irradiation

was characterized by higher density and lower roughness as shown in Table 1 and Fig.2. Such compact and dense PPy film may be a better barrier for ingress of chloride ions, which are responsible for breakdown of the passive oxide film.

More effective protection of the PPy coating is, therefore, interpreted by high doping level of $\text{PMo}_{12}\text{O}_{40}^{3-}$ ions and improved structural properties obtained by polymerization under ultrasonic irradiation.

5. Summary and conclusions

The effects of ultrasonic irradiation during electropolymerization of pyrrole in phosphoric acid containing $\text{PMo}_{12}\text{O}_{40}^{3-}$ ions on corrosion prevention of the polypyrrole coated steel were found as follows:

- i) The corrosion resistance of steel coated by the PPy film was improved by ultrasonic irradiation during electropolymerization of PPy. The time maintaining the passive state for the steel coated by PPy film prepared under ultrasonic irradiation is one and a half times as long as that for the steel coated by PPy film without ultrasonic irradiation.
- ii) The surface morphology of PPy film was changed with imposition of ultrasound in electropolymerization process. Under the irradiation, a dense and compact PPy layer was formed which was assumed to result from change in nucleation-growth mechanism with the ultrasound imposition.
- iii) The doping level of $\text{PMo}_{12}\text{O}_{40}^{3-}$ ions was increased twice by ultrasonic irradiation during the electropolymerization

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Table 1 Ratio of thickness to electricity, d/Q , and density, ρ , (ratio of mass to thickness) of the PPy films

Electropolymerization conditions	d/Q	ρ
	$\mu\text{m cm}^2/\text{C}$	g/cm^3
Without ultrasonic irradiation	2.1	3.4
Under ultrasonic irradiation	2.3	3.9

Table 2 Ratio of mass to charge, $\Delta m/\Delta Q$, and doping levels of counter anions in the PPy film

	$\Delta m/\Delta Q$ (mg C ⁻¹)	Doping level of $\text{PMo}_{12}\text{O}_{40}^{3-}$ ions, y_1	Doping level of HPO_4^{2-} ions, y_2	Number of Py units per one doped $\text{PMo}_{12}\text{O}_{40}^{3-}$ ion, $1/y_1$	Number of Py units per one positive charge, $1/x$
Without ultrasonic irradiation	0.69	0.044	0.097	23	3.1
Under ultrasonic irradiation	1.06	0.092	-	11	3.7

Fig. 1. The relationship between the mass of deposited film and the charge passed during the electropolymerization of Py in $\text{H}_3\text{PMo}_{12}\text{O}_{40} + \text{H}_3\text{PO}_4$ solution (Δ) under ultrasonic irradiation, and (O) without ultrasonic irradiation.

Fig. 2. FE-SEM micrographs of the PPy films electrosynthesized a) without ultrasonic irradiation and b) under ultrasonic irradiation in $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ + H_3PO_4 + Py solution. PPy

films were electrodeposited at a constant current density of 1 mA cm^{-2} with electricity of a1, b1) 0.5 C cm^{-2} , a2,b2) 1.0 C cm^{-2} and a3,b3) 2.0 C cm^{-2} .

Fig. 3. GD-OES depth profile of the PPy coating electropolymerized at a constant current density of 1.0 mA cm^{-2} for 1000 s on steel substrate without ultrasonic irradiation.

Fig. 4. GD-OES depth profile of the PPy coating electropolymerized at a constant current density of 1.0 mA cm^{-2} for 1000 s on steel substrate under ultrasonic irradiation.

Fig. 5. Open Circuit Potential as a function of immersion time in 3.5 wt.% NaCl solution for the steel covered by the PPy film electrodeposited at a constant current density of 1.0 mA cm⁻² for 2000 s a) under ultrasonic irradiation, and (b) without ultrasonic irradiation.

Fig. 6. The intensity ratio of P/Mo from GD-OES measurements for the PPy coatings electropolymerized at a constant current density of 1 mA cm^{-2} on steel substrate a) under ultrasonic irradiation, and b) without ultrasonic irradiation.