



## Electrodeposition of Conducting Polymers on Copper in Nonaqueous Media by Corrosion Inhibition

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### ABSTRACT :

This study demonstrates the direct anodic electrodeposition of polypyrrole (PPy), poly(3,4-ethylenedioxythiophene) (PEDOT), and polythiophene (PTh) on Cu electrodes by employing a corrosion inhibitor, succinonitrile (SN). SN was found to suppress anodic Cu dissolution beyond the oxidation potential of the polymer monomers. It is also revealed that the Cu surface passivated by SN is still adequately conductive to allow the redox reaction of 1,4-difluoro-2,5-dimethoxybenzene (FMB) and the oxidation of the polymer monomers. Through both cyclic voltammetry and galvanostatic techniques, PPy, PEDOT, and PTh films were successfully synthesized on Cu electrodes in the presence of SN, and the redox behaviors of the films were evaluated.

**Keywords:** Electrodeposition, Conducting polymer, Copper, Succinonitrile

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### 1. Introduction

Conducting polymers (CPs) have various potential applications such as microelectronics, organic electronics, photovoltaic cells, and energy storage devices.<sup>1-5)</sup> The electropolymerization of CPs, a versatile method to synthesize CPs, has been extensively studied.<sup>6-9)</sup> While the electropolymerization of CPs has been carried out mostly on noble metal electrodes (Pt, Au, glassy carbon), only a little progress has been achieved in the deposition on less noble substrates such as steel, Al, and Cu.<sup>10-16)</sup> This is because the anodic electrodeposition on the active metal is hampered by the metal oxidation that competes with the oxidation of the polymer monomer. Meanwhile, some appropriate anions (oxalate, tartrate, salicylate) have been revealed to allow deposition of polypyrrole (PPy) films on steel and Cu electrodes.<sup>10-16)</sup> The protective layer that the anions form on the electrode surface was

claimed to prevent massive dissolution of metal substrates.<sup>14-16)</sup> Employing a redox mediator such as Trion (4,5-dihydroxy-1,3-benzenedisulfonic acid) has been reported to lower the deposition potential and offer an effective way to prepare PPy film on Al and Al alloy.<sup>17,18)</sup>

All the previous strategies, however, are based on aqueous media and are not applicable to poly(3,4-ethylenedioxythiophene) (PEDOT) and polythiophene (PTh). This is because the synthesis of PEDOT and PTh, owing to their high deposition potentials, should be performed in nonaqueous media, but the carboxylate and sulfonyl-based chemicals are hardly soluble in nonaqueous solutions.

In this study, we demonstrate that the direct anodic electrodeposition of PPy, PEDOT, and PTh on Cu electrodes in nonaqueous solutions is possible with the aid of succinonitrile (SN) as a corrosion inhibitor. The CP films were obtained using both the potentiodynamic and the galvanostatic modes, and the redox properties of the films were examined. To the best of our knowledge, this is the first report on the direct

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electrodeposition of PEDOT and PTh on Cu electrodes.

## 2. Experimental

### 2.1. Chemicals

Reagent grade pyrrole (Py), 3,4-ethylenedioxythiophene (EDOT), thiophene (Th), succinonitrile (SN), and 1,4-difluoro-2,5-dimethoxybenzene (FMB) were purchased from Aldrich. Battery grade 1 M LiPF<sub>6</sub> in ethylene carbonate (EC) / diethyl carbonate (DEC) (1/2, v/v) were used as the base electrolyte solution.

### 2.2. Electrochemical measurements

A standard three-electrode configuration was employed for the electrochemical experiments. Either a Pt disk (area = 0.02 cm<sup>2</sup>) or a Cu disk (area = 0.20 cm<sup>2</sup>) was used as the working electrode. Prior to testing, the Pt electrode was polished with 0.3 μm alumina and the Cu electrode was abraded down to a 1200 grit SiC paper. Li foil and Pt wire were used for the reference and the counter electrodes, respectively. Electrochemical experiments were carried out with an EG&G Princeton Applied Research model 273A. All the experiments were performed in an Ar atmosphere glove box where H<sub>2</sub>O and O<sub>2</sub> concentrations were kept below 5 ppm and the temperature was held at 25±2°C.

## 3. Results and Discussion

### 3.1. Copper passivation by succinonitrile

The inhibition effect of succinonitrile (SN) on the Cu oxidation has been investigated by employing the linear sweep voltammetry (LSV) as shown in Fig. 1. In the base electrolyte without SN, the oxidation current rises steeply above 3.5 V, which is obviously due to the massive Cu oxidation. In sharp contrast, a current peak is observed around 3.0 V and further oxidation of Cu is significantly suppressed in the presence of SN. Similar inhibition behavior has been reported for the Cu oxidation in aqueous oxalate solutions, in which the current peak is ascribed to the formation of a passive copper oxalate layer on the Cu surface to suppress further oxidation.<sup>14,15</sup> However, there has been no report yet on the “peak and passivation” behavior in nonaqueous solutions. At present, it is not clear yet whether the inhibition effect of SN is related to the formation of passive copper/SN compounds. It

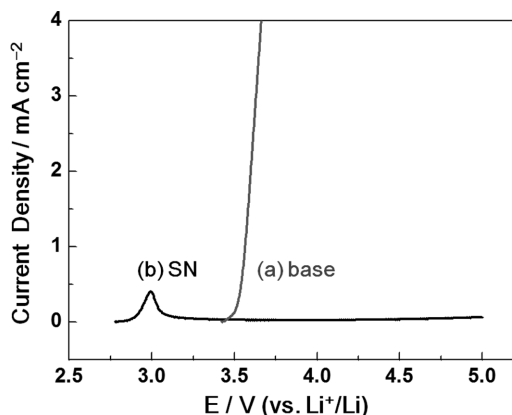


Fig. 1. LSVs of Cu electrodes in 1 M LiPF<sub>6</sub> EC/DEC (1/2, v/v) (a) without and (b) with 3 wt% SN. Scan rate = 20 mV s<sup>-1</sup>

is also possible that SN adsorbs on the Cu surface to form a passive layer, considering the fact that the open circuit voltage (OCV) of the Cu electrode is shifted from 3.4 V to 2.8 V by SN addition (Fig. 1). Besides the origin of the Cu corrosion inhibition effect of SN, it should be noted that the oxidation stability of the Cu electrode is extended at least up to 5 V in the presence of SN.

In order to examine the charge transfer behavior on the passivated Cu electrode, 1,4-difluoro-2,5-dimethoxybenzene (FMB) was employed as a redox probe. FMB exhibits quite a reversible CV on a Pt electrode with a formal potential at 4.5 V (Fig. 2(a)). The current rise above 5.0 V on Pt seems to be due to electrolyte decomposition. The redox behavior of FMB can also be confirmed on the Cu electrode that

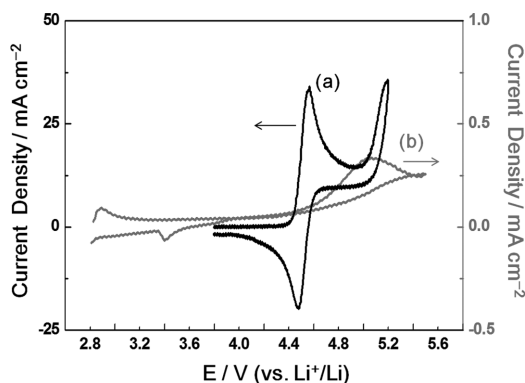


Fig. 2. CVs of 10 mM FMB in 1 M LiPF<sub>6</sub> EC/DEC (1/2, v/v) on (a) Pt electrode and on (b) Cu electrode scanned previously in 3 wt% SN solution. Scan rate = 20 mV s<sup>-1</sup>.

was previously scanned in the base electrolyte containing 3 wt% SN from OCV to 3.2 V passing a current peak at 3.0 V. The oxidation peak observed at around 5.0 V can be reasonably assigned to the oxidation of FMB, not to the electrolyte oxidation, since it is absent in the base electrolyte (Fig. 1). The small peak at around 3.4 V at the cathodic scan seems to be due to the reduction of the oxidized FMB. This indicates that the redox reaction of FMB is allowed on the Cu electrode passivated in a SN-containing solution, although its kinetics is quite sluggish. These findings encouraged us to try direct electrodeposition of the conducting polymers on Cu electrodes.

### 3.2. Electropolymerization of conducting polymers on Cu in a potentiodynamic mode

The oxidation behaviors of pyrrole (Py), 3,4-ethylenedioxythiophene (EDOT), and thiophene (Th) monomers on a Pt electrode were examined using linear sweep voltammetry (LSV) as shown in Fig. 3. The potential at which the oxidation current reaches  $0.05 \text{ mA/cm}^2$  was defined as the oxidation potential ( $E_{\text{ox}}$ ), and the values of the three monomers are summarized in Table 1. The  $E_{\text{ox}}$  of Py is determined to be 3.76 V, which is lower than those of EDOT (3.95 V) and Th (4.38 V). The order and the range of the  $E_{\text{ox}}$  values determined in this study are consistent with the previous reports.<sup>19</sup> When 3 wt% SN is introduced in the electrolyte, the  $E_{\text{ox}}$  value of Th is slightly increased by 0.1 V, but the other two are hardly altered. Irrespective of the presence of SN, dark black films are observed on the Pt surface after all the LSV experi-

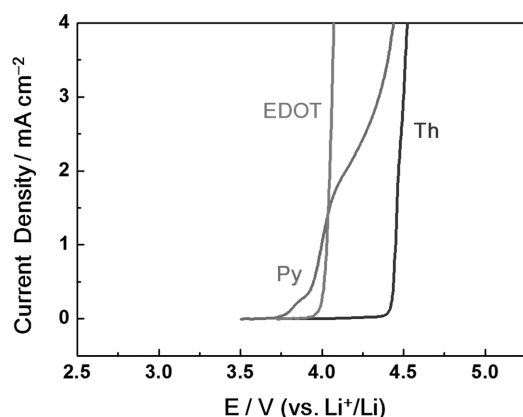


Fig. 3. LSVs of 0.1 M of monomer (Py, EDOT, and Th) in 1 M LiPF<sub>6</sub> EC/DEC (1/2, v/v) on Pt electrode. Scan rate = 20 mV s<sup>-1</sup>.

**Table 1.** Oxidation potential ( $E_{\text{ox}}$ ) of Py, EDOT, and Th on Pt and Cu electrodes.  $E_{\text{ox}}$  is defined as the potential where the oxidation current reaches  $0.05 \text{ mA cm}^{-2}$  in the LSV of 1M LiPF<sub>6</sub> EC/DEC (1/2, v/v) containing 0.1 M of monomer with and without 3 wt% SN

	Py	EDOT	Th
Base on Pt	3.76 V	3.95 V	4.38 V
Base on Cu	3.24 V	3.41 V	3.50 V
3 wt% SN on Pt	3.75 V	3.97 V	4.48 V
3 wt% SN on Cu	3.81 V	4.08 V	4.49 V

ments.

When the LSVs of the monomers are tried on a Cu electrode in the base electrolyte without SN, the  $E_{\text{ox}}$  values are rather independent of the monomer nature,

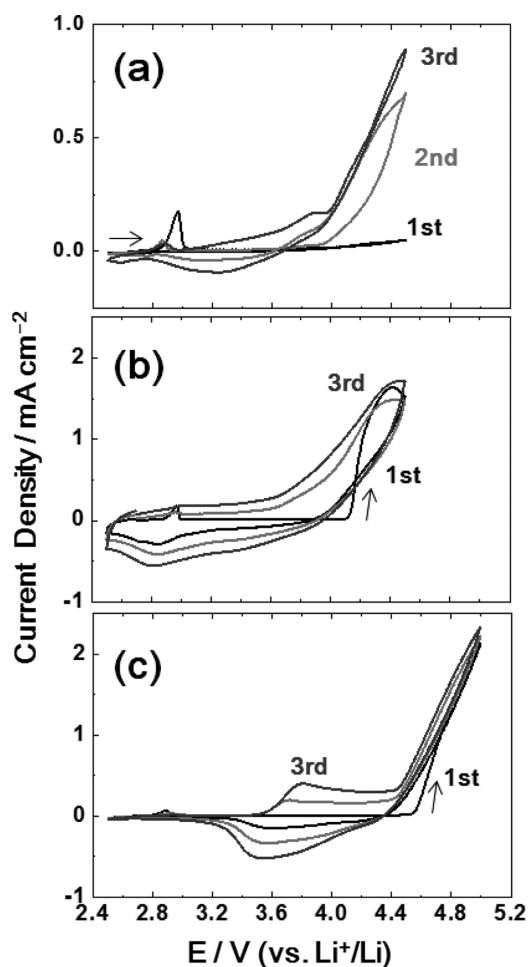


Fig. 4. Three consecutive CVs in 1M LiPF<sub>6</sub> EC/DEC (1/2, v/v) containing 3 wt% SN and 0.1 M (a) Py, (b) EDOT, and (c) Th. Cu working electrode. Scan rate = 20 mV s<sup>-1</sup>.

ranging from 3.24 V to 3.50 V (Table 1). No film formation was observed in this case, which indicates that the monomer oxidation is hampered by the concomitant Cu corrosion to preclude the electropolymerization. In contrast, the  $E_{\text{ox}}$  values of the monomers on Cu become similar to that on Pt in the presence of an SN additive. This implies that the monomer oxidation on Cu takes place in a similar manner to that on Pt.

Fig. 4(a) shows the cyclic voltammogram (CV) of a Cu electrode in 1M LiPF<sub>6</sub> EC/DEC (1/2, v/v) containing 3 wt% SN and 0.1 M Py. During the first three consecutive cycles, the current at the positive voltage limit keeps increasing. From the second cycle, the current increase over 2.8–4 V is appreciable, which indicates the formation of electroactive polypyrrole (PPy) film. In the case of EDOT, the oxidation current is larger than in the Py-containing solution, and the formation of poly(3,4-ethylenedioxythiophene) (PEDOT) is confirmed from the first cycle (Fig. 4(b)). The rapid growth of PEDOT film seems to be related to its relatively high electrical conductivity compared with PPy. The growth of poly(thiophene) (PTh) displays similar behavior to that of PEDOT (Fig. 4(c)). Note that the PTh film exhibits the typical conducting/insulating switching response, which manifest a decent quality of obtained polymer film.

### 3.3. Electropolymerization of polythiophene in a constant current mode

In order to qualitatively compare the properties of the polymer films deposited on Pt and Cu electrodes,

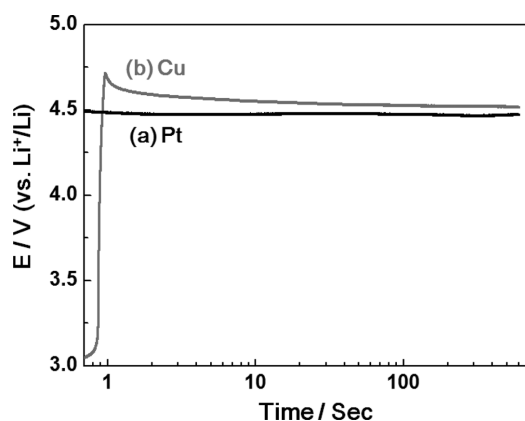


Fig. 5. Potential changes during galvanostatic deposition in 1M LiPF<sub>6</sub> EC/DEC (1/2, v/v) containing 0.1 M Th and 3 wt% SN on (a) Pt and (b) Cu electrodes. Current density = 2.5 mA cm<sup>-2</sup>.

the electropolymerization of PTh was performed both on Pt and Cu in the galvanostatic mode. The current density (2.5 mA/cm<sup>2</sup>) and the charge consumed during the electropolymerization (1500 mC/cm<sup>2</sup>) were fixed the same for both cases. Fig. 5 compares the potential changes for the galvanostatic deposition of PTh film on Pt and Cu in the presence of SN. On a Pt electrode, the potential/time response shows quite a flat behavior at around 4.47 V, which is close to the  $E_{\text{ox}}$  value of the Th monomer previously determined on Pt in the presence of SN (Table 1). Slight overshooting is observed in the potential/time curve on Cu with a short induction period (a couple of seconds). The potential is eventually stabilized at 4.51 V, which is also consistent with the previously determined  $E_{\text{ox}}$  value of Th monomer on Cu (Table 1).

After the galvanostatic polymerization, the films were transferred to the monomer-free base electrolytes and the five consecutive CV cycles were carried out (Fig. 6). The cathodic charges of both the films are

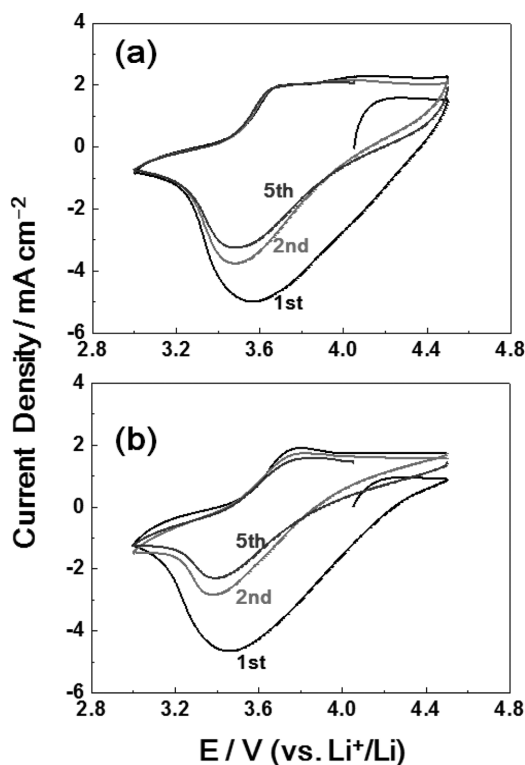


Fig. 6. Five consecutive CVs of PTh films in 1 M LiPF<sub>6</sub> EC/DEC (1/2, v/v) on (a) Pt and (b) Cu electrode prepared in Fig. 4. Scan rate = 200 mV s<sup>-1</sup>. Only 1st, 2nd, and 5th cycles are shown.

somewhat decreased and stabilized at the subsequent cycles, while the anodic charges are hardly altered with the cycles. Note that the redox behavior of the PTh film on Cu is quite similar to that on Pt, although the PTh on Cu shows a slightly reduced charge capacity. Considering the rather high loading/thickness of the PTh film and the fast scan rate employed in Fig. 6, the difference in the redox charges of the two films seem to be more kinetic in nature. In summary, the redox property of the PTh films deposited on a Cu electrode is quite comparable to that of the film on Pt.

#### 4. Conclusions

PPy, PEDOT, and PTh films were successfully electrodeposited on Cu electrodes in 1 M LiPF<sub>6</sub> EC/DEC (1/2, v/v) using an SN additive. SN served as a Cu corrosion inhibitor to extend the anodic stability of the Cu electrode beyond the oxidation potential of the polymer monomers. In addition, the Cu surface passivated by SN was found to be adequately conductive to allow the redox reactions other than the Cu oxidation. It was also found that the redox properties of the PTh films formed on a Cu electrode was quite comparable to those of the film on Pt. We believe this is the first report on the direct electropolymerization of PEDOT and PTh on Cu electrodes. The novel electrodeposition method developed in this study is expected to extend to any other materials, of which deposition potential is higher than that of the Cu oxidation.

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