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1-1-2014

## **Optimization of the sequential polymerization synthesis method for polypyrrole films**

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## Optimization of the sequential polymerization synthesis method for polypyrrole films

### Abstract

Polypyrrole (PPy) is widely used as an electroactive material and is most often synthesized using electrochemical polymerization. Recently, a new electropolymerization method [1] was introduced that involved preparing the PPy as a sequential series of electrodeposited layers with solvent washing in between each deposited layer. This method enabled high quality PPy free-standing films to be prepared in a relatively short time. The purpose of the present study was to investigate the effect of the polymerization current density on the mechanical and electrical properties of the sequentially polymerized (SEP) PPy films. It was found that a low current density (0.1 mA/cm<sup>2</sup>) and low temperature (-31 C) produced polypyrrole films of significantly higher conductivity and excellent mechanical properties when compared with films made at higher current densities either using the SEP method or by conventional, continuous electrodeposition.

### Keywords

films, method, synthesis, polymerization, polypyrrole, sequential, optimization

### Disciplines

Engineering | Physical Sciences and Mathematics

### Publication Details

Sangian, D., Zheng, W. & Spinks, G. M. (2014). Optimization of the sequential polymerization synthesis method for polypyrrole films. *Synthetic Metals*, 189 53-56.

# Optimization of the sequential polymerization synthesis method for polypyrrole films

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## Abstract

Polypyrrole (PPy) is widely used as an electroactive material and is most often synthesized using electrochemical polymerization. Recently, a new electropolymerization method [1] was introduced that involved preparing the PPy as a sequential series of electrodeposited layers with solvent washing in between each deposited layer. This method enabled high quality PPy free-standing films to be prepared in a relatively short time. The purpose of the present study was to investigate the effect of the polymerization current density on the mechanical and electrical properties of the sequentially polymerized (SEP) PPy films. It was found that a low current density ( $0.1 \text{ mA/cm}^2$ ) and low temperature ( $-31 \text{ }^\circ\text{C}$ ) produced polypyrrole films of significantly higher conductivity and excellent mechanical properties when compared with films made at higher current densities either using the SEP method or by conventional, continuous electrodeposition.

## 1. Introduction

Important applications for conducting polymers, such as artificial muscles [2], batteries [3], and sensors [4] require highly conducting and mechanically-robust free-standing films or fibers. Polypyrrole (PPy) has been widely investigated for these applications because of its relative ease of preparation as a free-standing film; reasonable stability; and good electrical and mechanical properties [5–7]. Electrochemical polymerization is the most common method used to prepare PPy films and the effect of electrochemical polymerization conditions such as temperature and deposition rate on the mechanical properties and conductivity has been studied for some time [7–10]. Smooth, non-porous films with high conductivity can be obtained through a slow, low-temperature electrodeposition process [11]. However, long synthesis times are required to generate free-standing films. Fast electrodeposition of PPy develops rough, porous films with reduced conductivity [8] and mechanical properties [9].

Recently, a significant reduction in the preparation time of PPy free-standing films without any compromise to the mechanical properties and conductivity has been demonstrated [1]. Films were prepared using a sequential electropolymerization (SEP) method involving a layer-by-layer electrodeposition with deposited polymer washed with solvent between each layer. It was shown

that solvent washing during the electropolymerization of pyrrole removed unbound oligomeric species from the deposited PPy [1]. Pyrrole oligomers are known to form during electropolymerization [7] and their presence within the deposited layer in rapid continuous electropolymerization appears to promote secondary precipitation of polymer particles and the formation of rough, porous films. In contrast, the SEP method produced smooth PPy free-standing films, with reasonable mechanical properties and high conductivity ( $220 \text{ S/m}$ ).

Studies to date have only considered the SEP method at mid to high current densities ( $>0.1 \text{ mA/cm}^2$ ) with the objective to reduce the synthesis time without compromising film properties. It is not known whether further improvements to the film properties could be achieved through the SEP method applied at low current densities and low deposition rates. The aim of this study, therefore, was to make a comparison of the SEP and continuous electropolymerization methods using different current densities.

## 2. Experimental

Tetrabutylammonium hexafluorophosphate (TBA PF<sub>6</sub>, Fluka), propylene carbonate (PC, Sigma-Aldrich), and ethanol of HPLC grade (Ajax) were used as-received. Pyrrole (Fluka) was distilled before use. The polymerization solution contained  $0.06 \text{ M}$  of pyrrole and  $0.05 \text{ M}$  of TBA PF<sub>6</sub> mixed in PC containing  $1 \text{ wt}\%$  of deionized water. Before the reaction commenced, the whole solution was purged with nitrogen gas for  $20 \text{ min}$  and cooled to  $-31 \text{ }^\circ\text{C}$ . A  $40 \text{ mm} \times 20 \text{ mm} \times 2 \text{ mm}$  (length  $\times$  width  $\times$  thickness) glassy

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carbon working electrode (SIGRADUR Hochtemperatur-Werkstoffe GmbH) was used as the substrate for electropolymerization of pyrrole. The counter electrode was reticulated vitreous carbon (RVC) foam (80 ppi). Polypyrrole was prepared via SEP and continuous electrochemical polymerization methods. Both methods use a constant current (galvanostatic). All the samples were polymerized at  $-31\text{ }^{\circ}\text{C}$ .

### 2.1. Electropolymerization

The total electropolymerization time was calculated according to the particular current density to ensure that the total charge passed was the same for each sample. The layer by layer sequential electropolymerization method involved preparing the free-standing film as eight separate polymerized layers with an ethanol wash between layers (Table 1). To wash the deposited PPy, the current was turned off, the working electrode removed from the electropolymerization cell and washed in a stream of ethanol. After drying with nitrogen gas, the electrode was returned to the cell and electropolymerization resumed.

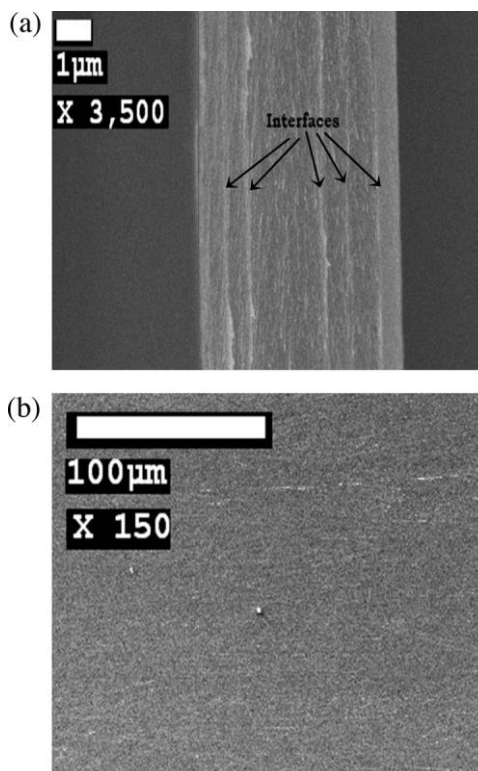
### 2.2. Film characterization

The PPy free standing-film thickness was measured via micrometer, SEM microscopy and profilometer. An optical profilometer (Wyko 9100) provided a precise thickness measurement of the PPy films. The average thickness was obtained by measuring the height of a cut edge of the film mounted on a glass slide. The film was first attached to the glass slide by double sided tape. Electron microscopy was performed with a JEOL JSM-7500 FA. For examination of free-standing film cross sections, samples were mounted in epoxy and sectioned by ultramicrotome. The cross sections were imaged by scanning transmission electron microscopy (STEM) which provided maximum contrast between PPy and the PPy-epoxy interface. Mechanical properties of the PPy free-standing films in the dry state were measured with EZS universal testing machine (Shimadzu). All samples were cut into strips approximately 2 mm wide and 15 mm long, and drawn at speed of 1 mm/min. The conductivity was measured by using a four-point probe (RM3, Jandel). Prior to those measurements, all PPy samples were carefully washed in ethanol to remove PC and then dried in a vacuum at  $35\text{ }^{\circ}\text{C}$  overnight. At least five identical samples were prepared and tested to assess the degree of variability. The reported mechanical and electrical properties were obtained from these dried samples. Actuation tests for PPy-PF<sub>6</sub> were performed in 0.25 M TBA PF<sub>6</sub> PC electrolyte using a conventional three-electrode setup. The three electrode arrangement allows for the accurate control of the applied electrochemical potential with respect to a reference electrode (silver/silver ion). The actuation stroke was measured using a lever arm (Aurora Scientific) force/distance transducer operated in constant force (isotonic) mode.

## 3. Results and discussion

### 3.1. Mechanical properties

Mechanical test experiments indicate that the sample polymerized continuously at  $0.1\text{ mA/cm}^2$  has the lowest elastic modulus and tensile strength of 0.40 GPa and 21 MPa, respectively (Table 2). The samples polymerized using the SEP method at different current densities ( $0.1\text{--}3\text{ mA/cm}^2$ ) exhibit similar elastic moduli and tensile strength in the range of (0.85–1.4 GPa and 40–65 MPa, respectively). Based on the previous work, it is known that PPy polymerized via SEP method at low temperature has a less porous structure with increased density and improved strength and modulus compared with continuously polymerized films [8,12]. Fig. 1



**Fig. 1.** SEM images of (a) cross-section, and (b) solution-side surface of a PPy free-standing film prepared using the SEP method at  $0.1\text{ mA/cm}^2$ .

shows the cross-sectional and surface microscopy images of PPy free-standing films. The surfaces of all SEP films were smooth and continuous and no micro-porosity was evident in the cross-sections. Interface junctions between sequentially deposited layers are noted in the cross-sections of all SEP films. The differences in the mechanical properties for the samples prepared via SEP method in this study are, therefore, not related to differences in porosity. Instead, it is possible that the films may have different crosslink densities with higher crosslinking resulting in a higher modulus.

### 3.2. Electrical conductivity

High electrical conductivity is a basic requirement for many applications for polypyrrole including actuators. The sample polymerized via SEP at  $0.1\text{ mA/cm}^2$  shows the highest conductivity of all samples at 500 S/cm. The conductivity tended to decrease for SEP films prepared at higher current densities. Significantly, the SEP films prepared at  $0.1\text{ mA/cm}^2$  had almost double the conductivity of the films prepared using the continuous, slow polymerization at the same low current density.

The higher conductivity of the SEP sample prepared at low current density suggests that this material has a higher doping level and/or an enhanced conjugation length, as these features are known to improve the conductivity of conducting polymers [13]. No difference was observed between the continuously and sequentially polymerized samples in terms of chemical composition (by Raman spectroscopy) or long-range order (by X-ray diffraction). Previous studies have noted a decrease in conductivity with increasing film thickness in electrochemically polymerized polythiophene films [14,15]. The decline in conductivity in these studies was attributed to a decrease in polymer conjugation length.

To demonstrate the usefulness of preparing PPy via the SEP method, films were evaluated as electromechanical actuators. Samples prepared at  $0.1\text{ mA/cm}^2$  by the continuous and SEP methods

**Table 1**

Washing conditions and average thickness of polypyrrole films polymerized at various current densities. (SEP: sequential electropolymerization; Cont: continuous electropolymerization).

Current density (mA/cm <sup>2</sup> )	Total electro-polymerization time	Number of layers	Electro-polymerization time for each layer	Washing solvent	Average thickness ( m)
0.10 (Cont)	8 h	1	8 h	None	9.65 ± 0.1
0.10 (SEP)	8 h	8	1 h	Ethanol	9.7 ± 0.1
0.50 (SEP)	96 min	8	12 min	Ethanol	9.55 ± 0.1
1 (SEP)	48 min	8	6 min	Ethanol	10.1 ± 0.1
2 (SEP)	24 min	8	3 min	Ethanol	10.2 ± 0.1
3 (SEP)	16 min	8	2 min	Ethanol	9.5 ± 0.1

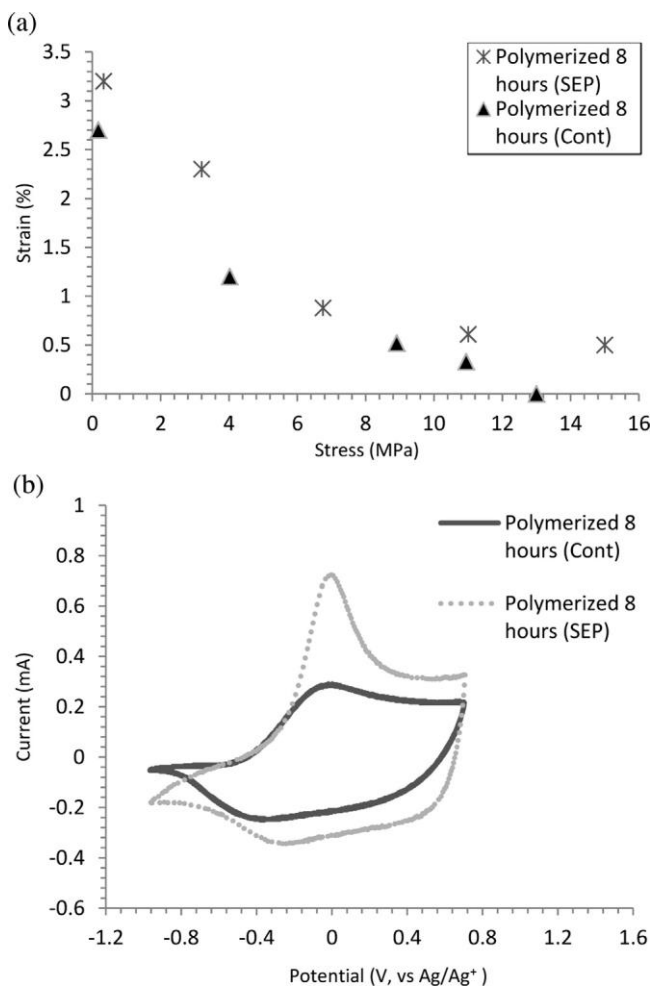
**Table 2**

Mechanical properties and electronic conductivity of PPy films prepared at various current densities.

Current density (mA/cm <sup>2</sup> )	Elastic modulus (GPa)	Tensile strength (MPa)	Electrical conductivity (S/cm)
0.10(Cont)	0.40 ± 0.05	21 ± 3.21	309 ± 0.80
0.10(SEP)	1.23 ± 0.10	47 ± 11.23	506 ± 0.77
0.50(SEP)	0.85 ± 0.04	50 ± 3.05	251 ± 0.48
1(SEP)	0.95 ± 0.04	65 ± 2.30	185 ± 0.80
2(SEP)	0.83 ± 0.12	44 ± 2.30	191 ± 0.99
3(SEP)	1.33 ± 0.05	38 ± 1.52	181 ± 0.80

were tested in isotonic actuation mode at various static stress levels. As shown in Fig. 2, the isotonic actuation strain decreases almost with the similar rate for both types of samples as the applied stress increases. The samples polymerized via SEP method represent a slightly higher electrochemical strain around 3.2% when compared

to the continuous sample when tested at small applied stresses (Fig. 2a). This increased actuation strain can be attributed in part to the improved electroactivity of the SEP films. For the sample polymerized via SEP at 0.1 mA/cm<sup>2</sup> the oxidation peak occurred at 0.02 V and the reduction peak was centered at 0.25 V. For the sample polymerized via the continuous method, the oxidation peak occurred at 0.01 V but reduction occurred at 0.40 V. The most significant difference in these cyclic voltammograms is the oxidation peaks of both samples showed different current densities (Fig. 2b). The maximum current density of the sample polymerized via the SEP method (0.7 mA/cm<sup>2</sup>) was significantly higher than the maximum current density obtained for the sample polymerized via the continuous method (0.3 mA/cm<sup>2</sup>). However, the maximum reduction current densities of both samples appeared almost the same, around 0.25 mA/cm<sup>2</sup> to 0.35 mA/cm<sup>2</sup>. The improved oxidation response of the SEP film compared to the continuous film is likely related to the higher conductivity of the former allowing easier electrochemical charge injection and higher currents.



**Fig. 2.** Artificial muscle performance: (a) actuation strain for isotonic actuation testing and (b) cyclic voltammograms.

#### 4. Conclusions

In conclusion, the experiments reported here indicates that the sequential electropolymerization method is able to produce superior PPy films in terms of mechanical properties and electrical conductivity as compared to continuous polymerization at a current density at 0.1 mA/cm<sup>2</sup>. The morphology, mechanical properties and electrical conductivity of the PPy samples polymerized via the SEP method were shown to be affected by the current density used. While previously it was shown that the SEP method at 3 mA/cm<sup>2</sup> could produce films of equivalent performance to continuously grown films at 0.1 mA/cm<sup>2</sup>, it has been shown in the present study that further improvements in properties can be achieved by SEP polymerization at low current density (0.1 mA/cm<sup>2</sup>). At this low current density the SEP method is no longer more time-efficient than the continuous polymerization. However, the improved properties can be important in certain applications.

#### Acknowledgements

The authors thank the Australian Research Council for partial funding of this work through its Centre of Excellence and Professorial Fellowship programs. The authors gratefully acknowledge the assistance of Mr. Tony Romeo and other staff of the University of Wollongong's Electron Microscopy Centre.

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