Electropolymerization of Polypyrrole on Carbon Electrodes: Effect of Pyrrole Concentration on Film Growth and Morphology

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Abstract: Polypyrrole (PPy) was electropolymerized onto round carbon electrodes (2.64×10^{-2} cm^2) using cyclic voltammetry (CV) as the electrodeposition method. The influence of pyrrole monomer concentration (0.005 M and 0.01 M) on PPy film growth and morphology was investigated to address shorting issues previously observed at higher concentrations on interdigitated electrodes (IDEs). During electrodeposition, cyclic voltammograms revealed that the oxidation of pyrrole follows diffusion-influenced mass transport, with higher oxidation currents at increased monomer concentrations. Electrochemical impedance spectroscopy (EIS) was used to characterize the interfacial properties of the resulting films and showed improved interfacial conductivity due to PPy deposition, even when the films were not visually apparent. These results demonstrate that controlled electropolymerization at lower monomer concentrations yields uniform, conductive PPy films, offering a promising strategy to mitigate overgrowth-induced shorting in microfabricated devices such as gas sensors, biosensors, and neural interfaces.

Key Words: Polypyrrole; Electropolymerization; Cyclic Voltammetry; Electrochemical Impedance Spectroscopy

1. Introduction

Conductive polymers, particularly polypyrrole (PPy), have emerged as promising materials for a wide array of applications, including sensors, actuators, and energy storage systems, due to their intrinsic conductivity, redox activity, and environmental stability (Borges et al., 2023; P. Li et al., 2023; X. Li et al., 2020; Ma et al., 2021; Tian et al., 2021; Wang et al., 2020). Among the various techniques available for film deposition, electropolymerization stands out as an effective method for forming PPy films on conductive substrates, offering precise control over characteristics such as thickness, morphology, and uniformity through the adjustment of electrochemical parameters (Borges et al., 2023). This control is crucial when tailoring materials to meet the performance requirements of specific applications.

However, depositing PPy onto interdigitated electrodes (IDEs)—common components in microscale sensors and biosensors—presents a significant challenge. The narrow gaps between IDE fingers make them highly susceptible to short-circuiting during electropolymerization, as overgrowth of the polymer can bridge the electrodes and render the device nonfunctional (Marek et al., 2021; Zheng et al., 2024). Controlled deposition is therefore essential to maintain device integrity, particularly for low-power or miniaturized electronic applications.

Building on previous observations in our laboratory, where higher pyrrole monomer concentrations (e.g., 0.1 M) led to PPy overgrowth into the gaps between IDEs, we aimed to address the issue of electrical shorting. Specifically, we investigated whether reducing the pyrrole concentration could enable more controlled deposition. To this end, we focused on two lower concentrations—0.005 M and 0.01 M—and evaluated their effects on film formation and electrochemical behavior using round carbon electrodes. The insights gained from this study will help optimize deposition protocols for PPy-based microscale devices, where precision in film thickness and electrode patterning is critical for performance.

2. METHODOLOGY

The electropolymerization of PPy was carried out on Polypyrrole (PPy) was electrochemically polymerized onto the working electrodes of EP-PP disposable electrochemical printed (DEP) chips from Biodevice Technology Incorporated. These DEP chips incorporate a three-electrode system consisting of a circular carbon working electrode (geometric area: 2.64×10^{-2} cm^2), an on-chip Ag/AgCl reference electrode, and an on-chip carbon counter electrode.

All electropolymerization experiments were performed using a BDT miniSTAT400 potentiostat (Biodevice Technology Incorporated). A 20 μL aliquot of the electropolymerization solution was drop-cast onto the DEP chips prior to polypyrrole (PPy) deposition. Two pyrrole monomer concentrations were tested: 0.005 M and 0.01 M. In both cases, 0.12 M sodium p-toluenesulfonate (Na-pTS) in Milli-Q water was used as the supporting electrolyte. Electropolymerization was carried out via cyclic voltammetry (CV). Due to the limited solution volume and the single-use nature of the DEP chips, each deposition consisted of a single potential cycle from 0 mV to 960 mV and back to 0 mV. To examine the influence of scan rate on film formation, the scan rate was systematically varied across experiments (10, 20, 30, 40, and 50 mV/s).

Electrochemical impedance spectroscopy (EIS) was performed on selected chips using a Hioki IM3590 Chemical Impedance Analyzer. EIS measurements were carried out over a frequency range of 100 kHz to 1 Hz, using 5 mM potassium ferricyanide ($[Fe(CN)_6]^{3-}$) as the redox probe. These measurements provided insight into the interfacial and charge transfer properties of the PPy-modified electrodes.

Additionally, prior experiments conducted with 0.1 M pyrrole on interdigitated electrodes (IDEs) frequently resulted in overgrowth and electrical shorting due to uncontrolled polymerization bridging the narrow electrode gaps. These observations highlighted the importance of optimizing monomer concentration for precise and reliable film deposition, particularly in microscale device architectures.

3. RESULTS AND DISCUSSION

3.1 Cyclic Voltammetry Analysis and Randles–Ševčík Behavior

Figure 1 shows the plot of the peak oxidation current (I_p) versus the square root of the sweep rate ($v^{1/2}$) for the electropolymerization of pyrrole at a 0.005 M monomer concentration (black squares), with the linear fit $y = 1.85044 + 5.96262x$.

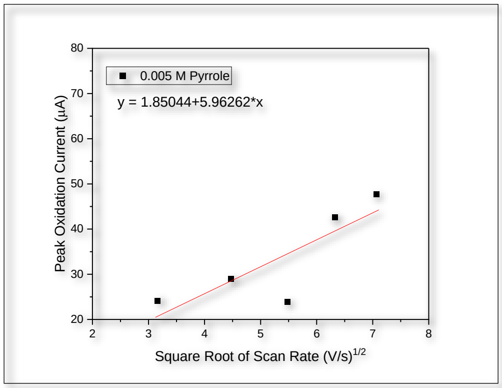

Figure 1. Peak Oxidation Current versus Square Root of the Scan Rate for the Electropolymerization of Pyrrole at 0.005 M

Figure 2 displays the corresponding plot for a 0.01 M monomer concentration (red squares), with the linear fit $y = -19.00568 + 12.84283x$.

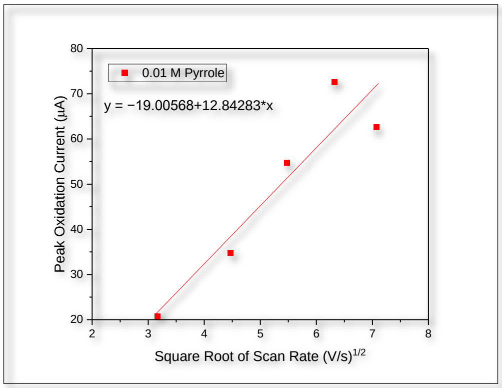

Figure 2. Peak Oxidation Current versus Square Root of the Scan Rate for the Electropolymerization of Pyrrole at 0.01 M

The Randles–Ševčík equation is commonly used to assess whether an electrochemical process is diffusion-controlled at a planar electrode (at 25 °C) and is given by:

$$I_p = (2.69 \times 10^5) n^{3/2} A C_{bulk} D^{1/2} \nu^{1/2} \qquad \text{(Eq. 1)}$$

where:

I_p = peak current (A)
n = number of electrons transferred
A = electrode area (2.64×10^{-2} cm^2)
C_{bulk} = bulk concentration (mol/cm^3)
D = diffusion coefficient (cm^2/s)
ν = scan rate (V/s)

The overall linearity observed in both Figures 1 and 2 suggests that diffusion governs the mass transport of pyrrole to the electrode surface at both concentrations.

Despite some scatter in the data for both concentrations, the linear trends support a diffusion-controlled process. Due to variability inherent in electrochemical measurements and the presence of scatter, absolute diffusion coefficients were not calculated. However, the observed increase in slope for the 0.01 M pyrrole (Figure 2) aligns with the Randles–Ševčík equation, which predicts higher peak current with increasing bulk concentration.

3.2 Electrochemical Impedance Spectroscopy (EIS) Analysis

Figure 3 presents Nyquist plots (0.1 Hz to 1 MHz) for the bare carbon electrode and electrodes modified with PPy using 0.005 M pyrrole at various scan rates (20, 40, and 50 mV/s). These plots show the relationship between the real part of the impedance (Z') on the x-axis and the negative imaginary part (-Z") on the y-axis, providing insights into the interfacial and charge transfer properties of the electrodes.

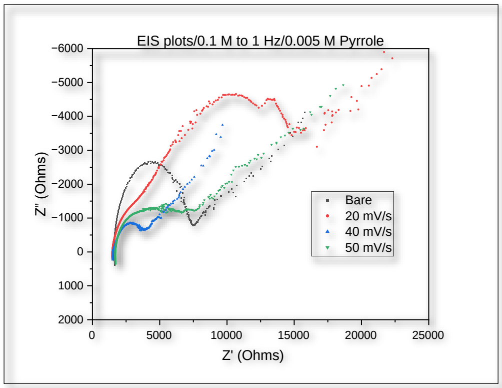

Figure 3. Nyquist plots (0.1 Hz to 1 MHz) for the bare carbon electrode and electrodes modified with PPy using 0.005 M pyrrole at various scan rates.

Even when a polymer film was not visibly apparent (as with the 0.005 M case, shown in Figure 4), EIS data revealed significant deviations from the bare electrode behavior, confirming the presence of an electroactive layer. This highlights the sensitivity of EIS in detecting thin or transparent conductive films.

Figure 4. Round working electrode of an EP-PP DEP chip after PPy deposition from 0.005 M pyrrole via CV at 40 mV/s.

For both concentrations, the Nyquist plots reveal a depressed semicircle at high to mid frequencies, typically attributed to surface roughness or heterogeneous charge transfer kinetics. Additionally, a linear region appears at lower frequencies, indicating diffusional limitations characteristic of Warburg impedance. When comparing the EIS results based on concentration, distinct differences are observed. At 0.005 M pyrrole, the electrodes exhibit relatively high impedance and broad semicircles, suggesting a higher charge transfer resistance (R_{ct}) as shown in Figure 3. In contrast, at 0.01 M pyrrole, the electrodes display lower impedance and smaller semicircles, indicating a lower R_{ct} and enhanced interfacial conductivity, as shown in Figure 5 below.

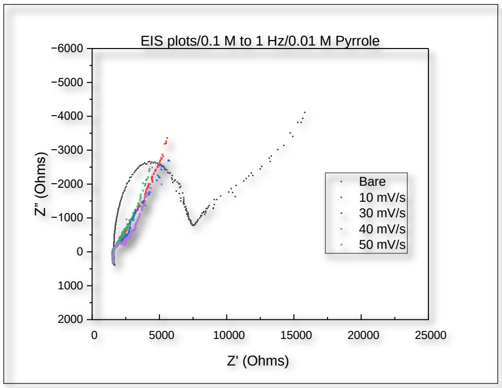

Figure 5. Nyquist plots (0.1 Hz to 1 MHz) for the bare carbon electrode and electrodes modified with PPy using 0.01 M pyrrole at various scan rates.

The lower R_{ct} observed at 0.01 M corresponds with the higher peak oxidation currents extracted from CV-based kinetic analysis (Figures 1 and 2), supporting faster electron transfer kinetics at the higher monomer concentration. The presence of Warburg impedance at low frequencies in both EIS datasets confirms that diffusion of pyrrole or ionic species continues to play a role during electropolymerization.

3.3 Impact of Pyrrole Concentration on Film Growth and Morphology

Figure 6 shows the overgrowth of polypyrrole (PPy) on a round carbon working electrode of an EP-PP chip after electropolymerization at a high pyrrole concentration (0.1 M). The image captures a thick, uneven PPy deposit extending toward the gap between the working and counter electrodes. Such overgrowth can interfere with microscale device functionality by increasing the risk of unintended electrical connections and instability.

Figure 6. Overgrowth of PPy on a round carbon working electrode of the EP-PP chip when using 0.1 M pyrrole monomer for the electropolymerization solution

In contrast, the more controlled deposition observed at 0.005 M and 0.01 M (supported by EIS in Figures 3 and 5) resulted in thinner and more uniform conductive films. In these lower-concentration cases, even electrodes that appear visually uncoated (as seen in Figure 5) are functionally modified, as evidenced by impedance measurements.

The slower polymerization kinetics at reduced monomer concentrations likely contribute to this improved control over film growth, mitigating the excessive accumulation seen at 0.1 M (Figure 6). These findings emphasize the importance of monomer concentration as a key parameter in balancing film uniformity, electrochemical activity, and long-term electrode stability.

4. CONCLUSIONS

This study highlights the critical role of pyrrole monomer concentration in governing the electropolymerization behavior of polypyrrole (PPy), influencing both film morphology and electrochemical performance. While prior work in our lab identified overgrowth and shorting issues at high monomer concentrations (e.g., 0.1 M) on interdigitated electrodes (IDEs), this investigation focused on systematically evaluating lower concentrations—0.01 M and 0.005 M—using three-electrode chips with round carbon working electrodes. At these reduced concentrations, film deposition was more uniform and controlled, significantly reducing the risk of overgrowth.

Electrochemical analysis using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) confirmed that pyrrole oxidation is influenced by diffusion-controlled mass transport, and that monomer concentration affects both electron transfer kinetics and interfacial properties. Notably, EIS detected improvements in interfacial conductivity due to PPy films even when no visible coating was observed—demonstrating the sensitivity of this technique in characterizing thin or transparent conductive layers.

These findings underscore the importance of optimizing monomer concentration for reliable and reproducible PPy deposition, particularly in microscale device fabrication. The results provide a foundation for future work aimed at extending these optimized conditions to more complex electrode architectures such as IDEs, with potential applications in multi-layer sensing platforms, flexible bioelectronics, and other microscale technologies

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