Electrochemical Deposition of Polypyrrole on Disposable Electrochemical Printed Chips

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Abstract: The demand for portable and wearable electronic devices necessitates miniaturized and flexible energy storage solutions. For high-power demands in such devices, microsupercapacitors are essential. Polypyrrole (PPy) is a promising material for microsupercapacitor electrodes due to its low-cost fabrication, high conductivity, and other desirable properties. This study focuses on electrochemically depositing PPy onto commercially available disposable electrochemical printed (DEP) chips for microsupercapacitor applications. Using cyclic voltammetry, PPy was successfully deposited on Interdigitated Carbon Electrode, Round carbon electrode, and round gold electrode substrates. Capacitance variations were observed, with the PPy-modified round carbon electrode showing the highest capacitance. This work demonstrates the feasibility of PPy deposition on DEP chips for microsupercapacitor applications.

Key Words: Pyrrole, Polypyrrole, Electrochemical Deposition, Cyclic Voltammetry

1. INTRODUCTION

The increasing demand for portable electronic devices has indeed fueled the necessity for miniaturized energy storage solutions, such as microsupercapacitors. Additionally, the growing popularity of wearable technology underscores the need for energy storage devices that are not just portable but flexible as well. To meet these evolving needs, researchers are exploring conducting polymer-based microsupercapacitors(Han & Dai, 2019; Wang et al., 2020; Zhang et al., 2022).

Among the various conducting polymers investigated for microsupercapacitor electrodes, polypyrrole (PPy) emerges as a particularly promising option. PPy is deemed a good candidate due to the ease and low cost at which it can be synthesized, its high conductivity, its high capacitance, its high cycling stability, and its ability to withstand high current densities (P. Li et al., 2023; X. Li et al., 2020; Ma et al., 2021; Tian et al., 2021; Wang et al., 2020).

PPy can be synthesized by different methods, but the most prominent methods are by chemical polymerization and electrochemical polymerization. In chemical polymerization, a stoichiometric amount of oxidant is used to induce the polymerization of pyrrole. On the other hand, in electrochemical polymerization, an electric current is applied on an electrode to cause the polymerization of pyrrole on its surface. While chemical polymerization is the older of the two methods, electrochemical polymerization has become more commonly used as it enables better control over polypyrrole film thickness and mass ratio, produces polypyrrole films with higher conductivity, and can synthesize PPy faster than chemical methods (Borges et al., 2023; Istakova et al., 2018)

In this work, PPy was electrochemically polymerized onto the working electrodes of commercially available disposable electrochemical printed (DEP) chips for potential microsupercapacitor applications. The small dimensions of working electrodes of 0.009 cm^2 for the interdigitated geometry and 0.0314 cm^2 for the round geometry necessitated modifications of the laboratory set-up commonly used for the electrodeposition of PPy on much larger electrodes. Potentiodynamic electropolymerization, or Cyclic Voltammetry (CV), was chosen as the electropolymerization technique as such method can produce nanostructured morphologies (Gvozdenovic et al., 2014) for larger surface areas. The CV characteristics of the PPy-modified working electrodes were then compared by using a handheld potentiostat.

2. METHODOLOGY

DEP chips were obtained from from Bio-device technology (BDT) Limited Company, 923-1211 Ishikawa-ken, Nomi City, Asahidai Ishikawa Creating Laboratory 106, as is shown in Figure 1. As is seen in the figure, three different types of chips were used: (a) a DEP chip with an interdigitated carbon working electrode (ICE), (b) a DEP chip with a round carbon working electrode (RCE), and (c) a DEP chip with a round gold electrode (RGE). Each chip features an Ag/AgCl reference electrode. They share a standard size of 12 millimeters in total length and 3 millimeters in total width. The interdigitated electrodes on the ICE chip consist of 9 digits, each measuring 1 millimeter in length and 0.1 millimeters in width, separated by a 0.05-millimeter gap. Meanwhile, both the round carbon and round gold electrodes have diameters of 2 millimeters.

Electrodeposition of PPy on the chips was done by Cyclic Voltammetry in a three-electrode system at room temperature and low light condition under nitrogen environment at a scan rate of 20 mV/s, at a voltage range of 0 - 0.80 V, for 8 cycles, and with vigorous stirring. The polymerization solution consisted of 0.1 M pyrrole monomer (Fujifilm Wako), 0.12 M Sodium *p*-toluenesulfonate (Na p-TS) (Aldrich) as dopant, and 0.1 M Zinc Oxide (Sigma Aldrich) as co-dopant in 50 mL distilled water. The electropolymerization was done using an SRS EC301 Potentiostat/Galvanostat.

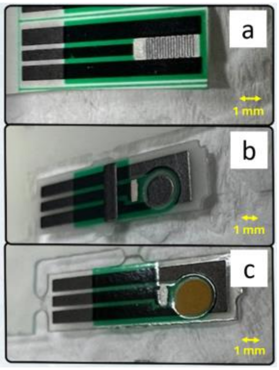

Figure 1. Tested Electrodes. (a) Bare ICE, (b) bare RCE, and (c) bare RGE DEP chips

CV characterization of the PPy-modified working electrodes were done by three electrode system using a BDT Ministat 100 hand-held potentiostat in 1 molar NaCl.

3. RESULTS AND DISCUSSION

Polypyrrole was successfully electrodeposited on the working electrodes of each DEP chip as is evident in the darker coloration of the working electrodes in each DEP chip in Figure 2.

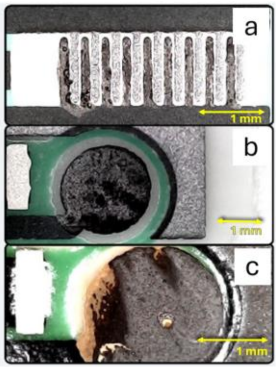

Figure 2. Magnified image of (a) ICE, (b) RCE, and (c) RGE DEP chips after PPy Electrodeposition

To evaluate the energy storage performance of the PPy-modified electrodes, cyclic voltammetry was performed in a three-electrode cell system using 1 M NaCl as the electrolyte. Figure 3 illustrates the CV curves of the PPy-modified ICE, RCE, and RGE electrodes versus the Ag/AgCl reference electrode, with a potential window of -0.2 to 0.4 V and a scan rate of 20 mV/s. Notably, the area enclosed by the CV curve of the PPy-modified ICE electrode appears smaller compared to that of the PPy-modified RCE and RGE electrodes. This discrepancy arises from the smaller geometric area of the interdigitated working electrode relative to the round working electrodes. Additionally, the CV curve of the PPy-modified RCE electrode exhibits a quasi-rectangular shape, indicative of electric double-layer capacitance behavior (Noori et al., 2019).

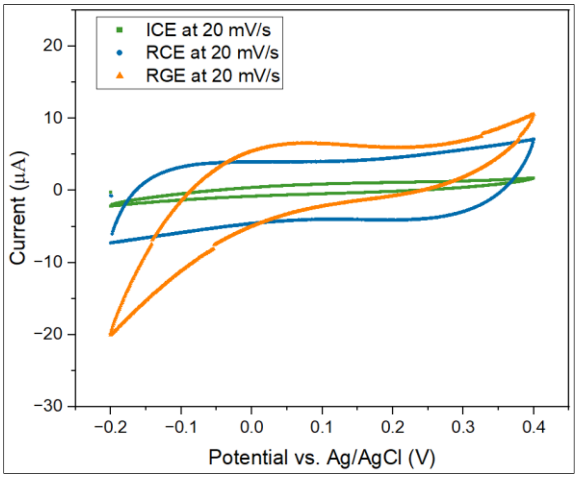

Figure 3. CV curves of PPy-modified ICE, RCE, and RGE electrodes vs. Ag/AgCl at a scan rate of 20 mV/s in 1 M NaCl

Figure 4 displays the CV curves of the PPy-modified ICE, RCE, and RGE electrodes relative to the Ag/AgCl reference electrode, with a potential window spanning from -0.2 to 0.4 V and a scan rate of 100 mV/s in 1 M NaCl. Notably, compared to the CV curves at 20 mV/s in Figure 3, those at 100 mV/s exhibit a more pronounced blunt and slanted shape, as anticipated at higher scan rates. This phenomenon is attributed to the overlapping effect of double-layer and pseudocapacitive charge storage mechanisms between the electrode's active materials and the electrolyte, along with a rise in the system's internal resistance (Noori et al., 2019).

Figure 4 also indicates that the area enclosed by the CV curve of the PPy-modified RCE is larger than that enclosed by the CV curve of the PPy-modified RGE. This finding aligns somewhat with the observation made by Tahir et al. (2023), who noted that the capacitance of an MSC with PPy-Carbon Nanotube (CNT) on reduced Graphene Oxide (rGO) electrode is greater than that of an MSC with PPy on a gold electrode. This difference may be attributed to the higher surface area of the PPy-CNT composite on rGO and its strong adhesion to rGO (Tahir et al., 2023).

Upon closer examination of Figure 3 and Figure *4*, it becomes evident that the area of the CV curve of the PPy-modified RGE is larger at 20 mV/s compared to its counterpart at 100 mV/s. This discrepancy could be attributed to the poor adhesion of gold on the carbon electrode, as evidenced in Figure 2c. It is plausible that the PPy film may have deteriorated after repeated CV scans, contributing to this difference

Moreover, Figure 3 and Figure *4* reveal that the area enclosed by the CV curve of the PPy-modified RCE deviates from its quasi-rectangular behavior at the higher scan rate of 100 mV/s.

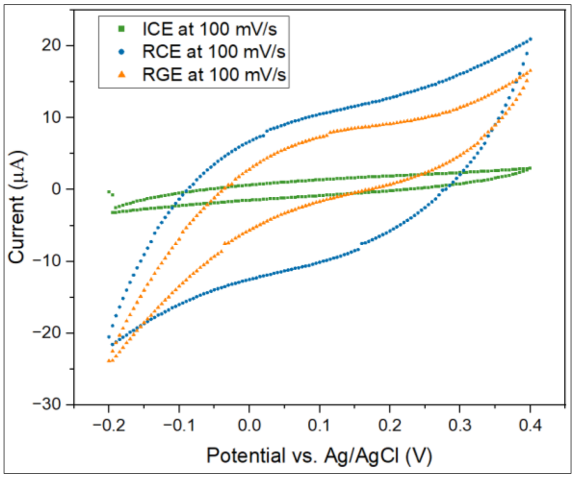

Figure 4. CV curves of PPy-modified ICE, RCE, and RGE versus Ag/AgCl at 100 mV/s in 1 M NaCl

The areal capacitance C_{areal} of the PPy-modified electrodes were estimated from the CV curves using

$$C_{\text{areal}} = \frac{1}{A\Delta Vr}\int_{V_1}^{V_2} idV \qquad (1)$$

where A is the geometric area of the working electrode, ΔV is the potential window, r is the scan rate, V_1 and V_2 are the initial and final potentials, respectively, and $\int_{V_1}^{V_2} idV$ is the area enclosed by the CV curve. The calculated areal capacitance using equation (1) at different scan rates are summarized in Table 1.

Table 1. Areal Capacitance of the Different Electrode Materials at 20 and 100 mV/s

DEP Chip	Areal Capacitance at 20 mV/s (milliFarad/cm^2)	Areal Capacitance at 100 mV/s (milliFarad/cm^2)
ICE	5.472	1.936
RCE	12.532	4.868
RGE	11.482	2.222

It can be seen from Table 1 that the PPy-modified working electrode of the RCE DEP chip exhibits the highest areal capacitance, which is at 12.532 mF/cm² at a scan rate of 20 mV/s and 4.868 mF/cm² at a scan rate of 100 mV/s. Additionally, the PPy-modified working electrode of the RGE DEP chip demonstrates an areal capacitance of 11.482 mF/cm² at a scan rate of 20 mV/s and 2.222 mF/cm² at a scan rate of 100 mV/s. Meanwhile, the PPy-modified working electrode of the ICE DEP chip yields an areal capacitance of 5.472 mF/cm² at a scan rate of 20 mV/s and 1.936 mF/cm² at a scan rate of 100 mV/s.

4. CONCLUSIONS

This preliminary study aimed to electrochemically deposit polypyrrole onto the working electrodes of commercially available screen-printed or digitally printed electrochemical (DEP) chips for potential microsupercapacitor applications. The working electrodes varied in terms of their geometry and composition. Electropolymerization was successfully achieved, and the results revealed notable differences in the capacitance values among the modified electrodes. Specifically, the PPy-modified interdigitated carbon electrode (ICE), with a significantly smaller geometric area compared to the round carbon electrode (RCE) and round gold electrode (RGE), exhibited a lower capacitance value of 5.472 mF/cm². Conversely, the capacitance of the PPy-modified RCE was notably higher at 12.532 mF/cm² compared to the capacitance of the PPy-modified RGE, which measured 11.482 mF/cm², despite having a similar geometric area. This preliminary work underscores the feasibility of electrodepositing PPy onto commercially available DEP chips.

5. ACKNOWLEDGMENTS

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