One-Step Electrodeposition of Lead Oxide Doped-Polypyrrole for 3D High Performance Supercapacitors

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Abstract. Supercapacitor electrodes comprising of conjugated conducting polymers (CPs) and metal oxides have become the focus of scientific research due to their high specific capacitance, low equivalent series resistance and high density with better cyclic stability. A 3D architecture is fabricated using polypyrrole and lead oxide as the building blocks by a facile, one pot chronoamperometry method to achieve a conductive additive free, binder free and scalable supercapacitor electrode. The superior electrochemical properties of the 3D PPy-PbO₂ are due to its porous structure, high surface area and high electrical conductivity that endow rapid transportation of electrolyte ions and electrons throughout the electrode matrix. The synergistic effect between the components in a proper ratio improves the supercapacitor performance and material stability. The structure and electrochemical performance of the 3D composite are correlated. The high specific capacitance (330 Fg⁻¹) and impressive cycling stability (>2000 cycles) estimated for PPy-PbO₂ open up an opportunity to consider the 3D nanostructures as cutting edge materials for energy storage solutions.

INTRODUCTION

The emerging demand for environment friendly and high performance supercapacitors often referred to as ultra capacitors or electrochemical capacitors, have been ever-increasing owing to the fossil energy crisis and the harmful environmental pollutions. Supercapacitors are battery-complementary energy storage devices capable of releasing large amount of energy in short time periods [1-3]. It provides outstanding power performance, excellent reversibility, very long cycle life, simple mode of operation, and ease of integration into electronics. In addition, they generate less thermochemical heat because of the simpler charge storage mechanisms associated. Therefore, they have been widely used in consumer electronics, memory back-up systems, and industrial power and energy management and will be found in more niche markets in the near future.

Metal oxides composites as electrode materials for supercapacitors have sought much attention in the recent years, because they are environmental friendly and cheap [4]. A facile co- electrodeposition method was developed by Chen et. al for fabricating the reduced graphene oxide/ polypyrrole (rGO/PPy) composite films, with sodium dodecyl benzene sulfonate as both a surfactant and supporting electrolyte in the precursor solution which showed superior electrochemical performance [5]. In 2017, Alves et. al synthesized a 3D structure composed of zirconia oxide nanoparticles (ZrO₂), reduced graphene oxide (rGO) and polypyrrole (PPy) which exhibited a capacitance of 341 Fg⁻¹[6]. In many hybrid supercapacitors PbO₂ has been effectively used as positive electrodes [7]. PbO₂ electrodes synthesized by electrodeposition methods showed high conductivity, excellent power performance and were chemically stable [8-10]. It is seen that the three dimensional porous structure enhances the supercapacitive performance for lead dioxide electrodes [11-14]. So, in our work, we have fabricated a novel 3D PPy-PbO₂ to investigate the supercapacitive behaviour and to the best of our knowledge there is no previous literature regarding this material.
EXPERIMENTAL

The 3D binary architecture PPy-PbO$_2$ was synthesized by electrodeposition method. In a typical procedure, 0.1 M of pyrrole (Sigma-Aldrich), purified by distillation, 7mM lead acetate (PbSO$_4$, 99%, Sigma Aldrich) and 0.1 M of sodium paratoluene sulphonate (NaPTs Sigma-Aldrich), in 50 ml water and was stirred for half an hour at room temperature. NaPTs is a supporting electrolyte cum doping agent for the electrochemical polymerization of pyrrole. Then this solution that acts as electrolyte was kept in a cyclic voltammetry pot. The electrodeposition was performed at constant potential of 0.8 V by employing a piece of carbon felt with an effective area of 2.5 cm$^2$ as working electrode immersed in the electrolyte under mild stirring. Ag/AgCl electrode and Pt wire were used as reference electrode and counter electrode respectively. The electrodeposition was performed for different durations of time from 30 minutes to 2 hour. The prepared electrode was heated in vacuum oven at 80°C for 12 hours.

RESULTS AND DISCUSSION

![Figure 1](image1.png)

**FIGURE 1.** XRD patterns for PPy-PbO$_2$.

Figure 1. shows the powder X-ray diffraction pattern of PPy-PbO$_2$. The peaks corresponding to (110), (101), (211) and (301) planes indicate the presence of PbO$_2$. The broadened diffraction peaks indicate the formation of small sized PbO$_2$ nanoparticles. The peak at 2θ =26° indicates the typical characteristic peak of PPy [13]. The formation of PPy-PbO$_2$ nanocomposite is confirmed by the XRD pattern of the sample.

![Figure 2](image2.png)

**FIGURE 2.** The SEM images of the electrodeposited PPy-PbO$_2$. 
The SEM images as in Figure 2 shows the morphology of the electrodeposited PPy-PbO$_2$. It reveals a thin coating of bulbous PPy polymer on carbon felt giving rise to a rough surface. The figure displays a network of porous interconnected 3D structure of PPy-PbO$_2$, which is electropolymerized onto the surface of the current collector. The PbO$_2$ are dispersed on the network of PPy forming 3D structures. The prepared 3D ternary architecture allows us to exploit the synergistic effects of the integrated components to the maximum and tap the best in achieving the superior properties.

![Image of SEM](image1.png)

**FIGURE 3.** CV curves of PPy-PbO$_2$.

The electrochemical performance of the novel 3D nanoarchitecture, PPy-PbO$_2$ is evaluated by cyclic voltammetry (CV), galvanostatic charge–discharge (GCD) and AC electrochemical impedance spectroscopy (EIS) using a standard three-electrode electrochemical cell containing 1M KCl electrolyte. The CV curves (Figure 3) show a deviation from the typical rectangular form which suggests the pseudocapacitive behavior of PPy and PbO$_2$. Electrochemical utilization due to the enhanced surface area especially the large ion accessible surface area facilitates rapid electronic and ionic transportation through the interface between electrode and electrolyte thereby provides more contact sites which account for the excellent electrochemical properties of PPy-PbO$_2$. Hence, this architecture is a promising candidate for the construction of high-performance supercapacitor electrodes with high stability.

![Image of Nyquist Plot](image2.png)

**FIGURE 4.** Nyquist plot of PPy- PbO$_2$.

Figure 4 gives the Nyquist plots of PPy-PbO$_2$ tested in 1 M KCl. At high frequency region, a small arc is observed which is related to the process at the electrode material-electrolyte interface and the low frequency region indicates a capacitive behavior related to the charging mechanism [4]. The EIS results indicate that the sample
possesses a lower charge transfer resistance and better capacitive behavior. The electron transfer resistance $R_{ct}$ of PPy-PbO$_2$ is only 2.0 Ω which suggests good conductivity and good ion transportation of the prepared PPy-PbO$_2$ electrode. These characteristics may be due to the synergistic effects and the ideal combination of the two components, which lead to a better capacitive performance for supercapacitors.

![Graph showing galvanostatic charge/discharge curves of PPy-PbO$_2$.](image)

**FIGURE 5.** The galvanostatic charge/discharge curves of PPy-PbO$_2$.

Figure 5 shows the galvanostatic charge/discharge curves of PPy-PbO$_2$ for the first cycle at a current density of 1 Ag$^{-1}$. It can be seen that all of the curves are linear and exhibit a typical triangular shape, which indicates good electrochemical capacitive characteristics. The triangular shape implies that charge is stored at the electrode-electrolyte interface. Specific capacitance of the electrode can be calculated from the charge–discharge measurements [1] using the formula:

$$C = \frac{It}{\Delta V.m}$$

where C is the specific capacitance of the electrode material, I is the constant discharge current, t is the discharge time, m is the mass loading of the active material and $\Delta V$ is the potential window during discharge. The specific capacitance of PPy-PbO$_2$ is found to be 330 Fg$^{-1}$ at a current density of 1 Ag$^{-1}$. This enhanced electrochemical activity is attributed to the synergy among the involved materials PPy and PbO$_2$ and better stability offered by the lead oxide during the cycling process.

**CONCLUSION**

Electrodeposition has been proven to be an effective method to prepare a PPy-PbO$_2$ nanocomposite film, which has the potential for real application as a supercapacitor electrode material. Even though the presence of PbO$_2$ increased the electron transfer resistivity between the electrolyte and ternary nanocomposite, it impedes the deterioration of the nanocomposite caused by continuous expansion and contraction during the charge/discharge cycles. PbO$_2$ contributes high capacitance and stability to the nanocomposite and offered a specific capacitance of 330 Fg$^{-1}$ at a current density of 1 Ag$^{-1}$, thus allowing the nanocomposite to manifest as a quality electrode material for supercapacitors.

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