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PPy@MWCNT Nanocomposite for Supercapacitor Applications

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Abstract – Polypyrrole (PPy) is a potential electrode material for supercapacitors due to its properties such as high conductivity and chemical stability. However, additional additives can be used to further improve the capacity values and energy storage performance of PPy. Multi-walled carbon nanotubes (MWCNT) are nanomaterials with properties such as high surface area, excellent conductivity and mechanical strength, and can improve supercapacitor performance when integrated into the PPy matrix. In this study, synthesis, characterization and performance analysis were performed to evaluate the potential of PPy and MWCNT doped PPy in supercapacitor applications. PPy and MWCNT doped PPy were characterized using analytical techniques such as XRD (X-ray diffraction) analysis and SEM (scanning electron microscopy) imaging. XRD analysis was used to determine the crystal structures and crystal sizes of the material and showed that the crystal structures of PPy and MWCNT doped PPy were preserved. SEM imaging was used to examine the surface morphology of the material and it was observed that it has a homogeneous surface structure. Supercapacitor performance was evaluated using electrochemical characterization methods. PPy and MWCNT doped PPy samples exhibited high capacitance values and fast charge-discharge properties. The integration of the MWCNT additive into the PPy matrix allowed the electrode to maintain its chemical stability while increasing the surface area. These results show that PPy and MWCNT doped PPy have the potential to provide more efficient energy storage in supercapacitors.

Keywords – MWCNT, PPy, PPy@MWCNT, Energy Storage, Supercapacitors

I. INTRODUCTION

Energy has been an indispensable element for the survival of living beings from the past to the present. With conscious human utilization, energy has become not only essential for survival but also a input used and developed in daily life with the advancement of technology [1]. Modern technologies demonstrate that everything around us is created through the utilization of energy [2]. The depletion of fossil fuels poses a significant concern for the long-term sustainability of energy resources. Fossil fuels are used in various fields such as electricity generation, heating, transportation, and industry worldwide. Therefore, the depletion of fossil fuels can lead to a major crisis in energy supply. As a result, increasing the use of renewable energy sources, enhancing energy efficiency, and implementing strategies such as energy conservation are seen as important measures against the risk of depleting fossil fuels. These developments are shifting the focus towards renewable energy [3]. Renewable energy refers to energy sources derived from solar, wind, hydro, geothermal, biomass, and other sources. The use of renewable energy offers several advantages over energy derived from fossil fuels. The use of renewable energy ensures energy security due to its potential to be an unlimited resource, unlike fossil fuels. Unlike fossil fuels, renewable energy sources are replenished through natural cycles and are not subject to depletion [4]. The use of fossil fuels in energy consumption and production significantly impacts the world economy and ecology.

Consequently, there is an increasing demand for environmentally friendly, high-performance renewable energy storage devices. Examples of such devices include batteries and supercapacitors. Batteries are devices composed of electrochemical cells that allow for the chemical storage and release of energy. Lithium-ion batteries are used in various applications ranging from portable devices to residential and industrial lighting [5]. Supercapacitors are one of the energy storage methods and offer potential solutions for many applications due to their high energy density and fast charge-discharge characteristics [6]. Supercapacitors store electromagnetic energy using an electrolyte solution between electrodes. Many different materials can be used in supercapacitor electrodes, with common materials including carbon, graphene, metal oxides, and polymers [7]. Supercapacitors have significant application value and market potential as a new energy storage device due to their environmentally friendly nature and excellent performance. They can be used in various fields such as industrial control, power, transportation, smart devices, consumer electronics, national defense, communication, defibrillators, pulse lasers, new energy vehicles, and more [8,9]. The materials used in the fabrication of supercapacitors are also crucial [10]. Pyrrole is a five-membered hydrocarbon and a heteroaromatic compound. Different derivatives of pyrrole are naturally found in many life forms. Due to the unique chemical properties of the compound, it has applications in various fields such as synthetic chemistry, pharmaceutical research, polymer science, and materials science [11]. Synthetic pyrrole, which can be obtained, has the ability to form materials that are electrically conductive, durable, and chemically stable. Pyrrole and its derivatives have a wide range of applications due to their high solubility in both polar and nonpolar solvents [12]. They are used in sensors, transducers, electrochemical devices, batteries, biomedical engineering applications, and many other industrial fields. Polypyrrole (Ppy) is one of the most extensively researched polymers in the pyrrole family and is considered an attractive material for sensor, electrochemical, and battery applications. Polypyrrole (Ppy) is a polymer that provides secondary electrochemical capacity through electrochemical interactions [13-14]. Therefore, Ppy is widely used in supercapacitor applications. Multi-walled carbon nanotubes (MWCNTs) are also used in the fabrication of supercapacitors. MWCNTs are highly important materials in the field of nanotechnology. They have numerous industrial applications, particularly in electronics, materials science, and biomedical fields. The properties of MWCNTs are characterized by their mechanical strength, chemical inertness, high thermal and electrical conductivity, high surface area, and many other features [15]. The results of this study demonstrate that PPy and MWCNT-incorporated PPy are a significant step in supercapacitor applications. These materials have the potential to provide high capacitance values, fast charge-discharge characteristics, and cyclic stability. PPy and MWCNT-incorporated PPy encourage further research to develop more efficient and reliable supercapacitor devices in the field of energy storage.

II. MATERIALS AND METHOD

A. *Materials and Equipment*

Ni foam, pyrrole, MWCNT, and $FeCl_3.6H_2O$ were employed in their analytical purity, without any additional pretreatment. All the reagents utilized in the experiments were procured from Sigma-Aldrich Co. LLC. The reactions were conducted using the ZIVE SP1 potentiostat-galvanostat electrochemical method.

B. *Preparation of Nickel Foams*

The nickel foams were cut into pieces with a diameter of 2 cm and a width of 1 cm. After being soaked in acetone for 5 minutes in a Petri dish, they were washed with ethanol for 5 minutes and then left to dry in an oven. The weights of the nickel foams to be used were measured and recorded.

C. *Synthesis of PPy and Preparation of MWCNT@PPy films*

Firstly, the prepared nickel foams were positioned inside microwave synthesis cells. In one of the cells, pyrrole monomer (0.5M) was introduced along with 0.5M $FeCl3 \cdot 6H2O$. In a different cell, pyrrole monomer and $FeCl3 \cdot 6H2O$ were added in equal proportions, and 10% MWCNT was included to form the polymer on it. Contrary to the previous cells, 20% MWCNT was added to the other cell. All the cells underwent a 20-minute microwave-assisted hydrothermal synthesis at 700 W. Following the 20-minute period, the cooled cells were opened, and the resulting PPy, PPy@10%MWCNT, and PPy@20%MWCNT-coated nickel foams were rinsed with distilled water and dried in a vacuum oven at 60°C.

D. *Electrochemical Measurements*

Cyclic voltammograms (CV) of the films were acquired employing a ZIVE SP1 potentiostat-galvanostat system equipped with a three-electrode configuration. The counter electrode consisted of a platinum (Pt) foil, the working electrode was composed of the fabricated films, and the reference electrode utilized was Ag/AgCl. The liquid medium employed was a 2M KOH redox electrolyte. Galvanostatic constant current (GCD) and cyclic voltammetry (CV) measurements were conducted utilizing this setup.

III. Results

A. *X-ray diffraction analysis*

XRD (X-ray diffraction) analysis is a technique used to determine the structural properties of PPy and MWCNT-doped PPy samples. XRD patterns allow analysis of crystal structures and crystal sizes. In Figure 1, XRD spectra of PPy, PPy@%10MWCNT and PPy@%20MWCNT nanoparticles are shown. The XRD pattern observed in the PPy samples indicates that there are prominent peaks. These peaks indicate the nature of the crystal structure of PPy. The characteristic peaks for PPy generally correspond to the crystallographic surface of PPy (020), with a 2θ value of about 25°. When the XRD pattern is examined in MWCNT-doped PPy samples, both characteristic peaks of PPy and peaks of MWCNT can be observed. It is noticed that there is no change in the intensity of the PPy peaks, while the MWCNT peaks appear as additional peaks. This indicates that MWCNTs participate in the PPy matrix and persist without affecting the crystal structure. The peak widths obtained from the XRD patterns provide information on crystal size and crystal regularity. Sharper peaks indicate better crystal regularity and smaller crystal sizes, while broader peaks indicate lower crystal regularity and larger crystal sizes. These XRD analysis results show that the crystal structures of PPy and MWCNT-doped PPy samples are preserved and the MWCNT doping is successfully integrated into the PPy matrix. This information helps to better understand the structural properties of the relevant samples and to interpret the supercapacitor performances.

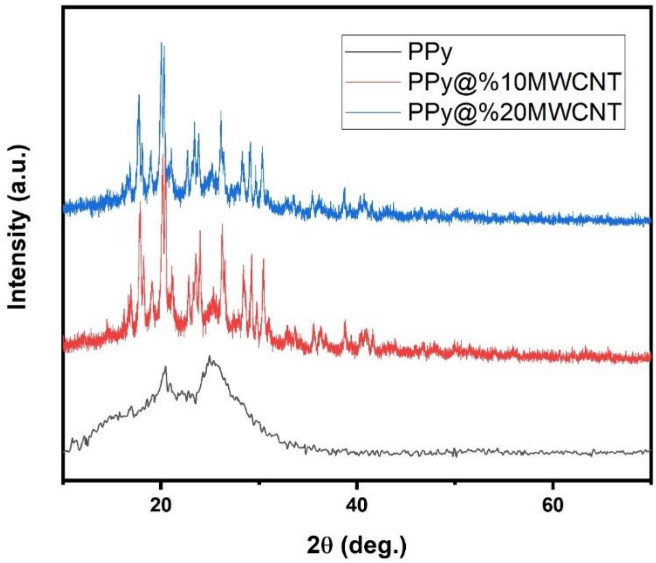

Figure 1. XRD pattern of nanoparticle of PPy, PPy@%10MWCNT and PPy@%20MWCNT

B. *Microstructure SEM and EDX analysis*

SEM imaging is a technique used to study surface morphology. SEM imaging of PPy and MWCNT-doped PPy samples is important to evaluate the nanostructures and distributions of these materials. SEM images of PPy, PPy@%10MWCNT and PPy@%20MWCNT nanoparticles are shown in Figure 2. When the SEM image of PPy samples is examined, a homogeneous surface morphology is observed. This indicates that PPy has a uniquely good surface structure and reflects good crystal regularity. When the SEM image of MWCNT-doped PPy samples is examined, it is seen that MWCNTs are dispersed in the PPy matrix and PPy nanofibers interact with MWCNTs. It is observed that the MWCNTs are uniformly dispersed and wrapped around the PPy nanofibers. This indicates that the MWCNTs are successfully integrated into the PPy matrix, and the material combination increases the mechanical strength. These SEM analysis results show that the PPy and MWCNT-doped PPy samples have homogeneous morphology and good distribution. The MWCNT additive was successfully integrated into the PPy matrix without affecting the surface morphology. This information helps to better understand the structural properties of the relevant examples and to interpret the supercapacitor performance.

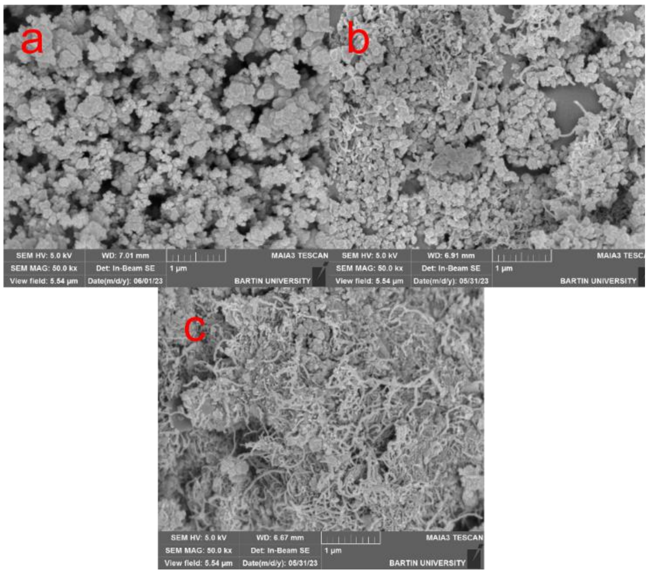

Figure 2. a) PPy, b) PPy@%10MWCNT and c) PPy@%20MWCNT SEM images

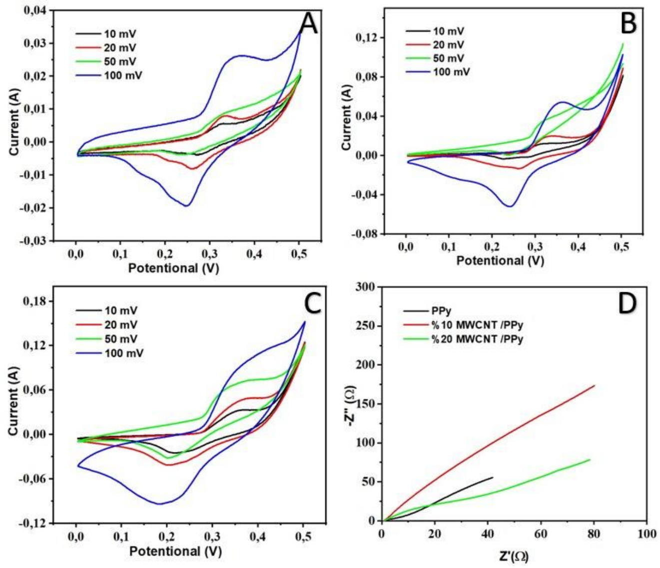

Figure 3. CV curves of a) PPy, b) PPY@%10MWCNT, c) PPY@%20MWCNT, EIS curves of d) PPy, PPY@%10MWCNT and PPY@%20MWCNT.

C. *Electrochemical Analysis*

Figure 3 (a-c) displays the cyclic voltammetry (CV) graphs for three different samples: bare polypyrrole (PPy), PPy/MWCNT10%, and PPy/MWCNT20%. The graphs cover a range of scan rates from 10 to 100 mV s^{-1} and a voltage range of 0 to 0.5 V. The presence of two redox peaks in the CV plots suggests that reversible Faradaic reactions take place within the electrode materials. Comparing the CV results according to the following formula, adding MWCNT makes an increase in the capacitance. This increase is supported by the EIS charts. The increase in surface area seen in SEM images also supports this situation.

$$C = \frac{area\ under\ CV\ curve}{scanrate.activemass.voltagerange}$$

IV. DISCUSSION

PPy and MWCNT-doped PPy are potential materials of great interest in supercapacitor applications. PPy's high conductivity and chemical stability make it a good electrode material for supercapacitors. MWCNTs, on the other hand, have high surface area, excellent conductivity and mechanical strength and can improve supercapacitor performance. The combination of PPy and MWCNT further improves supercapacitor performance. Integration of MWCNTs into the PPy matrix can transfer their high surface area and good conductivity to PPy. This provides more active surface area on the electrode surface and improves capacitance values by increasing electrochemical surface reactions. At the same time, the mechanical durability of MWCNTs increases the cyclic stability of the electrode and reduces the loss of performance over long periods of use. Studies have shown that PPy and MWCNT doped PPy exhibit high capacitance values and fast charge-discharge properties in supercapacitors. The MWCNT additive increases the electrochemical reaction rate by improving the surface properties of PPy, while maintaining the chemical stability of PPy. This indicates that PPy and MWCNT doped PPy can provide more efficient energy storage in supercapacitors.

V. CONCLUSION

This study demonstrates the significant potential of PPy and MWCNT-incorporated PPy in supercapacitor applications. When the high conductivity and chemical stability of PPy are combined with the high surface area and excellent conductivity of MWCNTs, it is observed that the resulting material can enhance supercapacitor performance. The synthesis and characterization of PPy and MWCNT-incorporated PPy were carried out using analytical techniques such as XRD and SEM. XRD analysis was employed to determine the crystal structure and size of the material, and the results showed that the crystal structures of PPy and MWCNT-incorporated PPy were preserved. SEM imaging was used to examine the surface morphology of the material, and it was observed to have a homogeneous surface morphology. The results of this study demonstrate that PPy and MWCNT-incorporated PPy are a significant step in supercapacitor applications. These materials have the potential to provide high capacitance values, fast charge-discharge characteristics, and cyclic stability. PPy and MWCNT-incorporated PPy encourage further research to develop more efficient and reliable supercapacitor devices in the field of energy storage.

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