ISSN No:-2456-2165 https://doi.org/10.38124/ijisrt/IJISRT24AUG1503

Supercapacitor Performance of in Situ Polymerization for PANI/MnO_2-TiO_2

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Abstract:- Manganese-titanium oxide particles coated with polyaniline (PANI) have been suggested as a highly favorable electrode material for supercapacitors. The synthesis of MnO_2-TiO_2 particles was achieved using the sol-gel technique, followed by calcination. The MnO_2-TiO_2 was mixed with pre-synthesized PANI to create a composite material called PANI/ MnO_2-TiO_2. The structural composition and purity of the produced materials were verified using X-ray diffraction (XRD). The morphological analysis conducted using field emission scanning electron microscopy (FESEM) revealed that particles are securely attached to the branched-structured PANI, facilitating rapid charge transfer. The electrochemical properties of MnO2-TiO2 and PANI/MnO_2-TiO_2 were analyzed using cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), 1 M H_2SO_4 electrolyte. PANI/MnO_2-TiO_2 demonstrated a substantial increase in specific capacity (1500 C/g) compared to PANI (450 C/g) at 1 A/g. This improvement can be attributed to the enhancement of redox-active sites and the synergistic interaction of the conductive PANI and MnO_2-TiO_2.

Keywords:- *Supercapacitor, MnO_2, PANI, Cyclic Voltammetry.*

I. INTRODUCTION

The study of supercapacitors, often called electric double-layer capacitors (EDLCs), is experiencing a significant surge in interest. This is mostly due to their exceptional performance as short-term power sources with high peak power capabilities. EDLCs store energy by utilizing electrostatic reactions (specifically non-Faradaic reactions) that occur between a thin layer of electrolyte separator and the surfaces of the electrode material [1-4]. The use of conductive carbonaceous materials, such as activated carbon [5], graphene [6], and carbon aerogel, is a widespread practice in this application. These materials can store energy at a significantly faster rate compared to traditional capacitors. This is because the materials have a large specific surface area, allowing them to quickly collect and release many electrolyte ions during the charging and discharging processes.

Regrettably, EDLCs are hindered by their low specific capacity, leading to a low energy density. This limitation restricts their use in applications that require consistent energy production over an extended duration. Researchers have been intensively studying the potential of hybrid supercapacitors to address this issue. These supercapacitors combine the characteristics of battery-type electrode materials with conducting carbonaceous materials to provide a synergistic effect [7-12]. In contrast to EDLCs, hybrid supercapacitors are composed of diverse electrode materials that are segregated by an electrolyte. Hybrid supercapacitors utilize EDLC-type materials for the negative electrode and battery-type materials, which store energy through Faradaic reactions, for the positive electrode. The objective is to attain a high energy density while maintaining a high power density by employing electrostatic and Faradaic processes within a single device. So far, manganese-based compounds, including manganese dioxides, manganese sulfides, and manganese carbonates, have been extensively studied as electrode materials for supercapacitors because of their strong redox characteristics. Nevertheless, using manganese phosphate as an electrode material for energy storage has yet to be extensively explored. MnO_2-TiO_2 has demonstrated outstanding efficacy in ceramic [13-16] and anticorrosion coating applications due to its affordability, strong ion exchange capacity, and remarkable chemical and thermal stability. Regrettably, like other compounds containing transition metals, MnO_2-TiO_2 has inadequate electrical conductivity, leading to a sluggish electron transport rate during electrochemical reactions. An effective solution to overcome the issue is combining MnO_2-TiO_2 with a substance with comparatively greater electrical conductivity. Therefore, polyaniline (PANI), a highly conductive substance with exceptional electrical properties (subject to the specific synthesis procedures and parameters), has been chosen. By adjusting the physicochemical characteristics of MnO_2-TiO_2 using the conductive PANI, it is possible to decrease the electrical resistance of the MnO_2-TiO_2 material. Furthermore, PANI can provide supplementary electroactive pathways for the transport of ions, enhancing the electrochemical reversibility in redox processes [17-23].

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II. EXPERIMENTAL

A 3 ml solution of aniline and 20 ml of 1 M HCl were combined in an ice bath with vigorous stirring. Following this, 20 ml of 1 M ammonium persulphate was slowly added to the acidic solution while continuously stirring. A black-green precipitate formed and was allowed to sit in the refrigerator for 24 hours. Subsequently, the precipitate was washed until it reached a neutral pH. Finally, the precipitate was dried at 70 °C for 3h. The producer was repeat by mixing separately 3ml aniline, (20 ml,1 M) HCl and 0.01g of MnO_2-TiO_2.

III. RESULTS AND DISCUSSION

➢ *Structural Characterization*

The structural properties of PANI/TiO2-MnO2 is investigated by XRD and FESEM. The XRD pattern of the as-synthesized polyaniline (PANI) is presented in **Figure 1**. The XRD analysis revealed the presence of two distinct peaks at 14.87, 20.87, and 24.98, corresponding to the (121), (113), and (322) crystallographic planes, respectively. These peaks were attributed to the periodic arrangement of PANI in directions perpendicular and parallel to the polymer chain, as reported by reference.

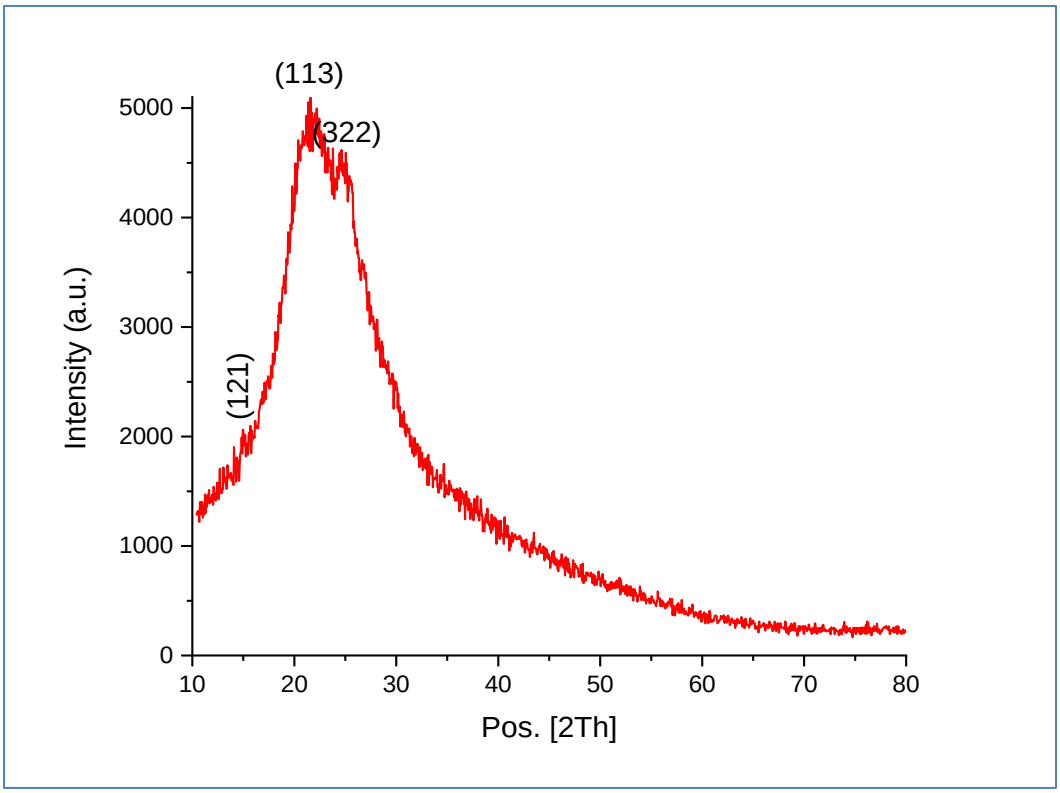

Fig 1 XRD of Polyaniline

The XRD pattern of the PANI/$MnTiO_4$ synthesized material is presented in **Figure 2**. Two distinct diffraction peaks corresponding to PANI were observed at 21.77 and 24.72, denoting the crystal planes (113) and (322), respectively. Similarly, two diffraction peaks at 29.42 and 36.66 were attributed to the crystal planes (310) and (211) of MnO_2. Furthermore, a prominent diffraction peak at 48.34 was identified, indicating the presence of crystalline planes (200) associated with the modified TiO_2.

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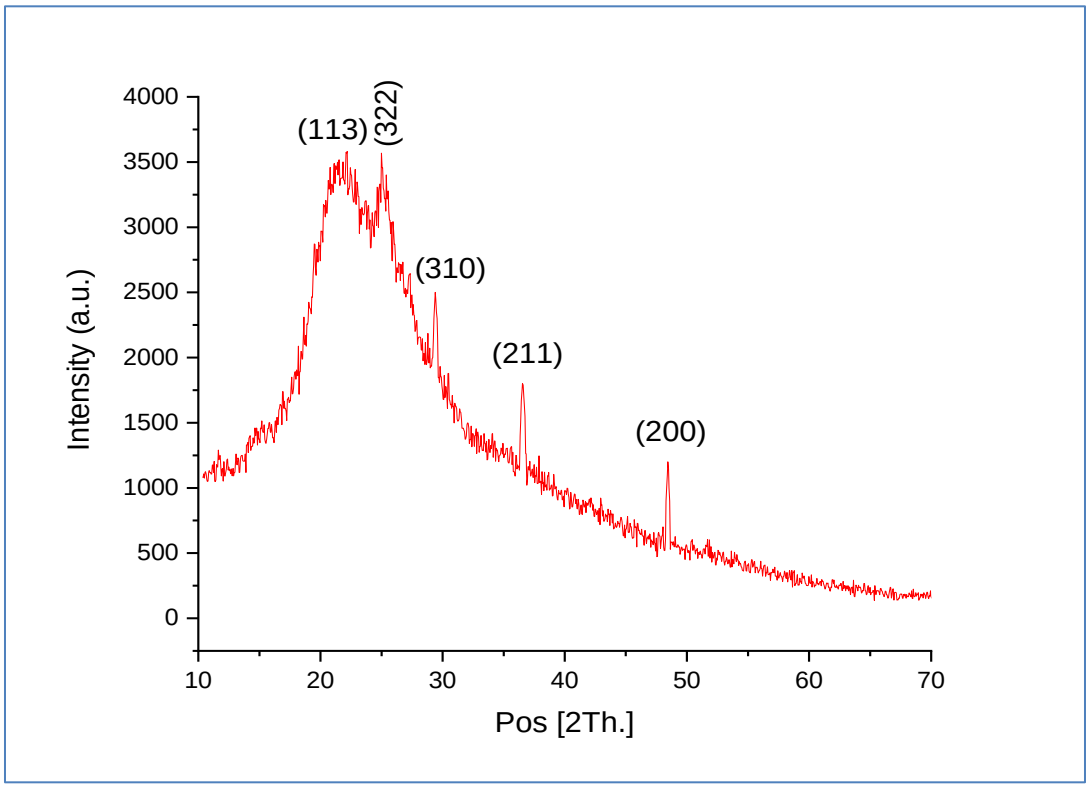

Fig 2: XRD of PANI/TiO_2-MnO_2

Figures 3 illustrate the field-emission scanning electron microscopy (FESEM) images of MnO_2-TiO_2 integrated into a polyaniline (PANI) nanocomposite. The images demonstrate the formation of PANI/MnO_2-TiO_2, with the agglomeration of oxides interacting with the PANI nanotubes and covering them, indicating successful in situ-polymerization processes.

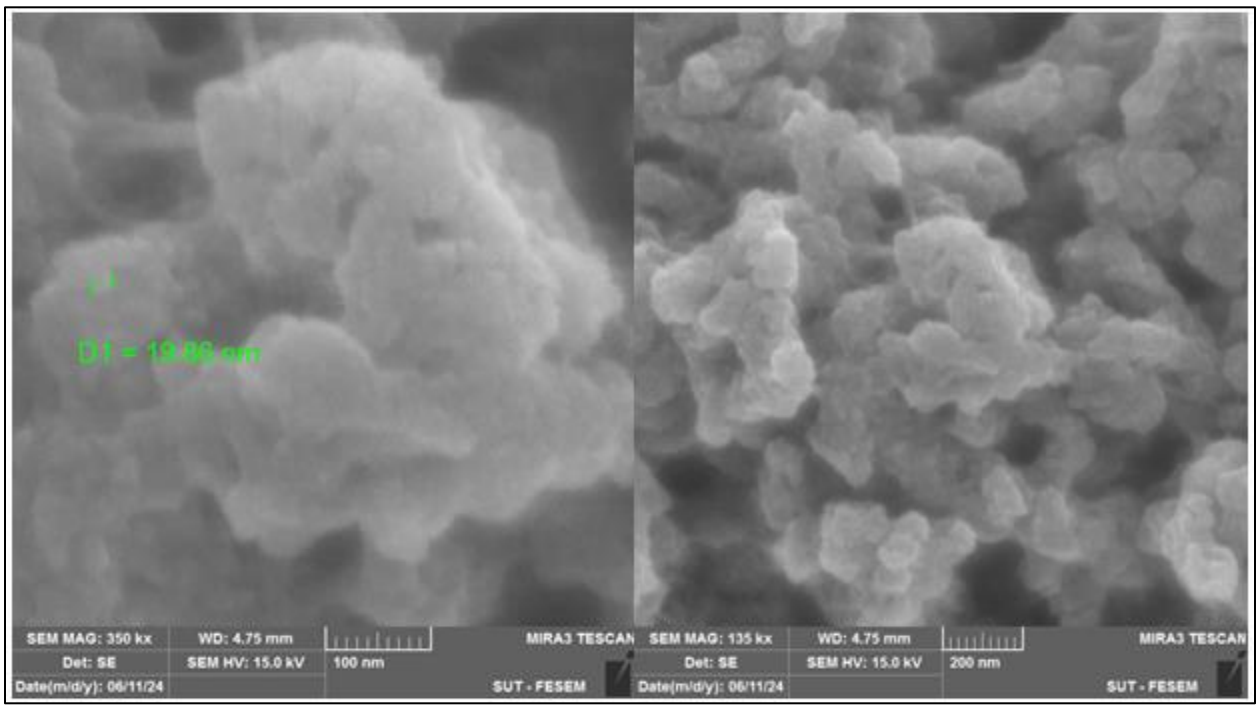

Fig 3: FESEM of PANI and PANI/MnO2-TiO2

ISSN No:-2456-2165 https://doi.org/10.38124/ijisrt/IJISRT24AUG1503

➢ *Electrochemical Properties*

The study conducted galvanostatic charge–discharge (GCD) cycles on PANI, TiO_2-MnO_2, and PANI/TiO_2-MnO_2 in a 1 M H_2SO_4 electrolyte solution, varying the current (0–10 mA) and potential (0–0.9 V). The outcomes are depicted in **Figures 4**. The charge–discharge curves (CD) display inversion mirror symmetry across all current values, indicating an increase in nonlinear behavior and strong electrochemical characteristics as a pseudocapacitive with increasing current density. The discharge time decreases as the voltage drop rises due to an increase in current density, as shown in **Figure 4**. Yu et al. (2020) calculated the specific capacitance from GCD curves using Equation 1.

$$Csp = \frac{I*t}{V*m} \quad 1$$

where m is the active material mass, I is the discharge current, Δt is the discharge duration, and ΔV is the potential window. The specific capacitance obtained from galvanostatic charge-discharge (GCD) measurements corresponds to different current densities, namely 1, 3, 7 and 10 mA, for PANI/MnO_2-TiO_2, TiO_2-MnO_2, and PANI. The specific capacitance values for these materials show significant differences across the various current densities. Notably, the addition of MnO_2-TiO_2 binary oxide to PANI led to an improved electrode structure as evidenced by the comparison of results. The findings underscore the importance of incorporating TiO_2-MnO_2 in creating new sites for energy storage and facilitating multiple carriers for electron transport within the electrode. The decreased internal resistance led to a notable enhancement in the electrode's efficacy for electrochemical reactions. Concurrently, it was noted that as current densities rose, the specific capacitance of the produced materials declined due to insufficient time for ions to access or reach the working electrode surface.

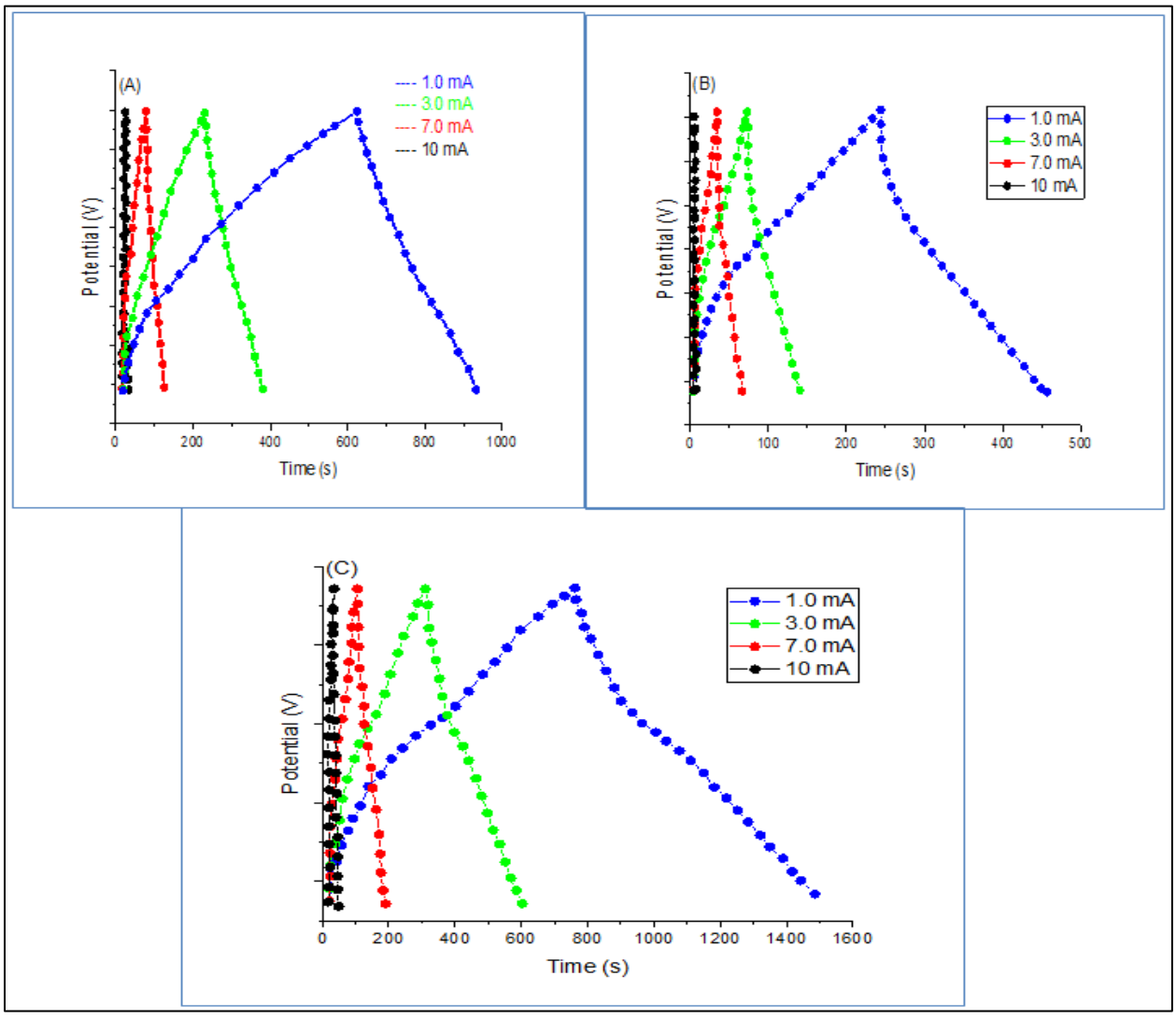

Fig 4: CP of PANI, TiO_2-MnO_2, and PANI/TiO_2-MnO_2

ISSN No:-2456-2165 https://doi.org/10.38124/ijisrt/IJISRT24AUG1503

This work showed how the introduction of a binary system affected the electrical properties of PANI by conducting cyclic voltammetry (CV) measurements on PANI, TiO_2-MnO_2, and PANI/TiO_2-MnO_2. The electrochemical measurements were performed using 1 M H_2SO_4 as the electrolyte solution. Separate experiments involved the use of three different electrode materials (PANI, TiO_2-MnO_2, and PANI/TiO_2-MnO_2) to investigate cyclic voltammetry. Cyclic voltammetry (CV) measurements were conducted at different scan rates within a potential window of 0–1.2 V, as depicted in **Figure 5**. **Figure 5a** presents the cyclic voltammetry data for PANI, TiO_2-MnO_2, and PANI/MnO_2-TiO_2 at a scan rate of 10 mVs^{-1}. The results exhibit a rectangular box shape for both electrodes, characteristic of an ideal supercapacitor with efficient charge transport. Additionally, the reduced contact resistance values indicate the pseudocapacitive nature of the electrode materials. After incorporating anatase TiO_2-MnO_2 into the PANI/TiO_2-MnO_2 matrix, the CV analysis of PANI/MnO_2-TiO_2 exhibits noticeable improvement compared to PANI and TiO_2-MnO_2, suggesting an increase in capacitance values at the same scan rate. The CV curves in (**Figure. 5b**) depict the performance of PANI, TiO_2-MnO_2, and PANI/TiO_2-MnO_2 at a scan rate of $20mVs^{-1}$. Even at high scan rates of 20 mVs^{-1}, the redox peaks associated with the transition between leucoemeraldine, emeraldine, and emeraldine pernigraniline states of PANI demonstrate exceptional performance for PANI/MnO_2-TiO_2. Moreover, the findings indicate a slight shift in the anodic and cathodic peaks, which is attributed to minimal electrode resistance. The reversible reaction between the active materials of electrodes and electrolyte interfaces in the presence of 1 M of H_2SO_4 results in changes in anodic and cathodic currents. This process, depicted in **Figure 5b**, leads to an increase in peak current separation with higher scan rates. Ghebache et al. (2021) employed a specific method to calculate the specific capacitance of PANI, TiO_2-MnO_2, and PANI/MnO_2-TiO_2 and calculated as following Equation 2.

$$Csp = \frac{A}{2\gamma m(V)} \qquad 2$$

where m is the active mass (g), (ΔV) is the potential window (V), and γ is the scan rate (V/s). The findings indicate that the modified PANI by TiO_2-MnO_2 (binary oxide) exhibits higher capacitance compared to TiO_2-MnO_2 and PANI. This is attributed to the presence of binary oxide, which--------h enhances the structure and facilitates electrolyte accessibility by increasing surface area and enhancing polymer-binary oxide interaction. Sandip et al. (2015) observed that at different scan rates, depicted in **Figure 5C**, capacitance values decrease with increasing scan rate due to the existence of an inner active site within the electrode, preventing the capacitance from surpassing the redox transition entirely. Cycling stability is an essential property for practical applications of supercapacitors. As depicted in **Figure 5d**, GCD measurement was employed to assess the cycling stabilities of PANI, TiO_2-MnO_2, and PANI/TiO_2-MnO_2 over 1000 cycles at a current density of $10A.g^{-1}$.The circular charge and discharge cycles, as well as the significant current, cause damage to the electrodes of both the pure binary system (TiO_2-MnO_2) and PANI. This indicates that the cycle stability of the binary system (MnO_2-TiO_2) and pure PANI is inferior to that of PANI/MnO_2-TiO_2. The MnO_2-TiO_2 nanocomposite exhibits minimal capacitance retention after 750 cycles, with a 75% retention for pure PANI at $10A.g^{-1}$. Conversely, the PANI/TiO_2-MnO_2 nanocomposite demonstrates robust cycling stability, retaining 91% of its initial capacitance after 1000 cycles, signifying the predominant contribution of binary oxide.

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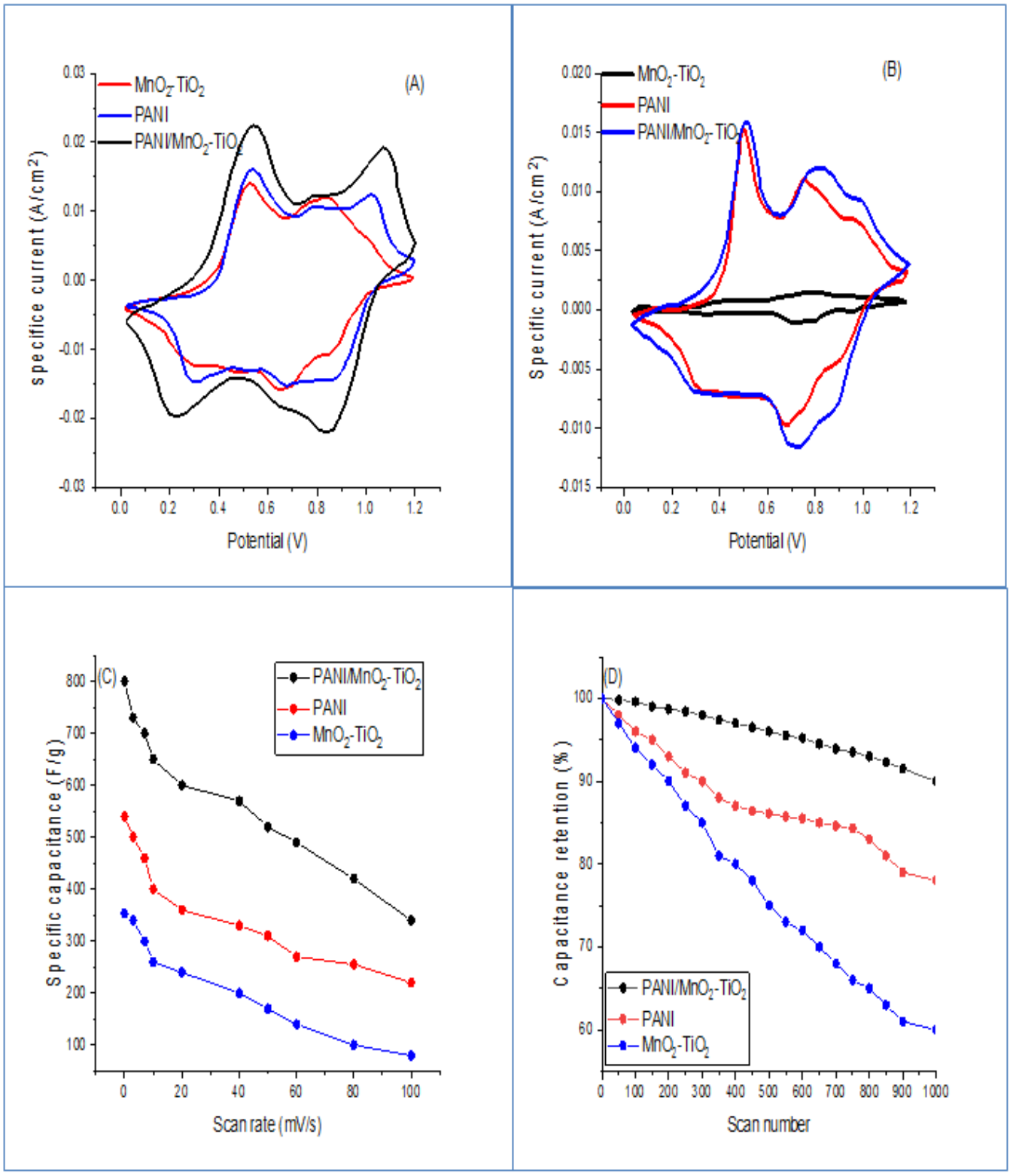

Fig 5: CV PANI, TiO_2-MnO_2, and PANI/MnO_2-TiO_2 at a Scan Rate (A) 10mV/s, (B) 20 mV/s, (C) Different Scan Rate and (D) GCD Measurement for 1000 Scan Number

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IV. CONCLUSION

The sol-gel approach was used to create several morphologies of the structure of MnO_2-TiO_2. Adding PANI to MnO_2-TiO_2 particles improved the electrochemical performance of MnO_2-TiO_2. The phase structure and content were analyzed using XRD. The electrochemical performance, as evaluated using cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) experiments, shows that the specific capacity of PANI is improved compared to pure MnO_2-TiO_2. In addition, the battery demonstrated excellent cycling stability, with a capacity retention rate of around 80% after undergoing 1000 charge-discharge cycles at a current density of 10 A/g. Therefore, the MnO_2-TiO_2 composite shows significant promise as a possible contender for energy storage applications.

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