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Research Article

Synthesis and Electrochemical Capacitor Characterization of Novel Composite Materials with p-Type Conductive Polymer

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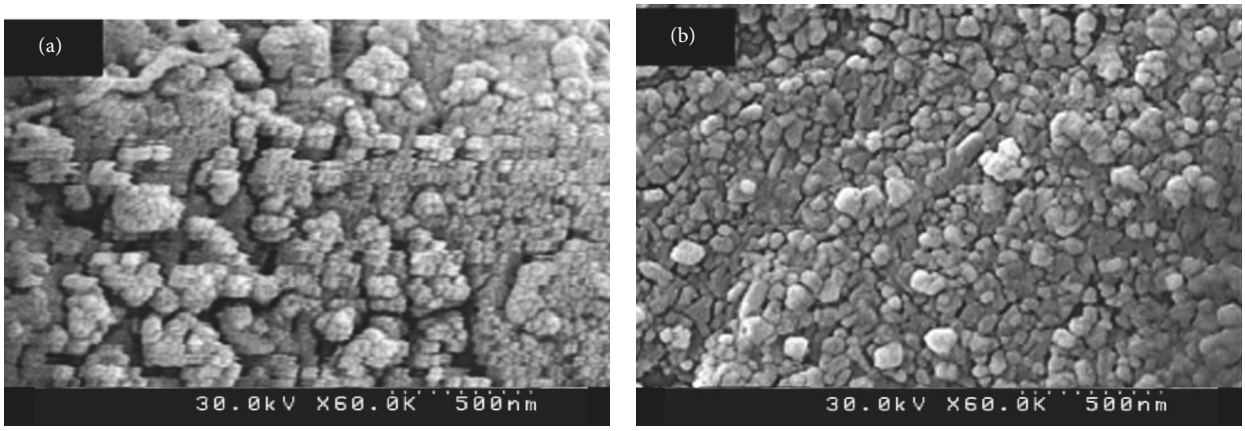
Considering the importance of conductive polymer nanocomposite, the present paper attempts to create a method for increasing the conductivity of poly(o-aminophenol). Nanocomposite MnO_2/poly(o-aminophenol) thin film was synthesized by using pulse potential electrodeposition technique on a graphite electrode. In this research, nanoparticles of MnO_2 are used after synthesis to prepare polymer nanocomposites in one-step. Appending of MnO_2 to polymer matrix increases the current. This current growth could be ascribed to the synergistic MnO_2 nanostructure, which presents the superior surface area and smaller particle size that is increasingly acting sites. Morphology or samples composition was investigated by the scanning electron microscope and the UV-Vis method, which clearly indicate the formation of nanocomposites. The findings show that the capacitive behavior of MnO_2-poly(o-aminophenol) is superior to poly(o-aminophenol), especially at high potential high temperatures. The results showed that MnO_2/poly(o-aminophenol) had a higher level of activity and the electron transfer capability was faster than pure polymer film. The doped MnO_2 polymer also has excellent cyclic performance and load discharge features. Additional electrochemical properties of these polymer composites were observed against pure polymer so that capacity of 645 Fg^{-1} has been designated.

1. Introduction

Over the past years, the study of polymers has attracted much attention and has many advantages such as simple synthesis, low cost, high chemical stability, adjustable doping /doping properties, and high conductivity [1–4]. Poly(o-aminophenol) is one of the best conductivity polymers and it has been of great interest to researchers whereas it is more excellent electrical conductivity [5, 6]. They have a diversity of usages like microelectronic devices, capacitors, transistors, corrosion protection, and chemical sensors [7, 8]. Ehsani et al. [9] have fabricated POAP/1-octadecyl-3-methylimidazolium bromide composite films as active electrodes supercapacitors and reported that the supercapacitor behavior of the composite film is due to the high active surface area, charge-transfer in the polymer chain, and synergistic efficacy amongst conductive polymer and [OMD] Br. In order to improve the performance of supercapacitors, many efforts have been done to incorporate metal oxides for polymerization, making composite electrode materials. Varaprasad et al. [10] have reported that metal-oxide polymer nanocomposite films are useful for the dielectric device and supportable energy harvesting applications. MnO_2 and its derivatives have attracted particular attention and are used in various applications such as catalysts, batteries, sensors, and batteries [11, 12]. Ozan Yanik and his colleagues [13] have been investigated magnetic conductive polymer/graphene nanocomposites for supercapacitors. They were able to achieve 255 Fg^{-1} specific capacitance values for it and they showed it has a healthy cell performance. Bahloul et al. [14] synthesized polypyrrole (PPy) deposited onto γ-MnO_2 particles. They concluded that PPy/MnO_2 composite has high specific capacitance of 141.6 F g^{-1} compared with 73.7 F g^{-1} for γ-MnO_2. It indicates that the improvement of the coating is due to the electronic conductivity of the polymer and an increase of the BET surface area that raises to 125m^2 g^{-1} after coating, against 64 m^2 g^{-1} for MnO_2. Hamid Mohammad Shiri and his colleague [15] have fabricated POAP/Dy_2O_3 films to serve as the active electrode for electrochemical supercapacitor. They found the enhanced supercapacitor behavior observed for the composite film could



(a) (b)

Figure 1: SEM images of (a) poly(o-aminophenol) and (b) MnO_2-poly(o-aminophenol) nanocomposite electrodes after using pulse potential electrodeposition technique synthesis.

be attributed to synergistic effect existing between Dy_2O_3 nanoparticles and the conductive polymer. Sydulu Singu et al. [16] have reported that PPy-Ag nanoparticles nanocomposite exhibits the specific capacitance of 266.7 F g^{-1} and the power density of 3998 W kg^{-1} and excellent capacitance after 5000 charge-discharge cycles, which determines the potential electrode material for supercapacitor application. Poly-o-phenylenediamine/MnO2 materials were synthesized by the addition of cetyl trimethyl ammonium bromide and sodium dodecyl sulfate [17]. Research results showed a high specific capacitance (262.2 Fg^{-1}) and a good electrochemical performance, making poly-o-phenylenediamine a promising material in supercapacitor application. However, a study on the synthesis of one-stage MnO_2/poly(o-aminophenol) nanocomposite and its capacitive behavior has not been done. Poly(o-aminophenol) is a p-type conductive polymer [18] that exhibits its maximal electroactivity within the potential range -0.2 V < E < 0.5 V versus (SCE). One of the effective methods for increasing its life cycle is combination of polymer and nanomaterial for the preparation of nanocomposite coatings for various applications. Manganese dioxide is widely used for the cheap metal oxides supercapacitor applications due to abundant in nature, high porosity, highly reversible chemical adsorption/desorption, good electrochemical performance, and environment-friendly [19, 20]. It is believed that the MnO_2 electrode capacity is mainly due to reversible changes that involve the exchange of protons and/or cations with the electrolyte [21, 22]. In this research amount of specific capacity for pure MnO_2 is 203 F g^{-1} for MnO_2. To improve electrical conductivity of the polymer and creation higher surface area, MnO_2 is mixed with poly(o-aminophenol), which increases the specific capacity.

Therefore, we proposed a one-step easy procedure for the synthesis of MnO_2 doped poly(o-aminophenol), in which doping of MnO_2 was achieved simultaneously during the electrochemical polymerization of o-aminophenol. In this paper, after synthesis of nanocomposites, the use of the MnO_2-poly(o-aminophenol) nanocomposite for capacitor applications with high performance is discussed.

2. Materials and Methods

2.1. Materials. The chemicals were prepared from Merck firm as the analytical grade. Electrochemical tests were carried out using a system three-electrode cellby a μ-Autolab potentiostat/galvanostat and a frequency response analyzer (Metrohm, Model 12/30/302, and The Netherlands). Graphite (G) with a diameter of 0.3 cm was applied as a worker electrode and platinum foil as an auxiliary electrode, while Ag /AgCl was operated as a reference electrode. The morphologies of the electrosynthesized conductive polymer obtained were investigated by field emission scanning electron microanalyzer model KYKY-EM3200.1.

2.2. Synthesis of MnO_2-Poly(o-aminophenol). MnO_2 nanoparticles were synthesized by reduction of 0.1 M $KMnO_4$ aqueous solutions with ethanol by ultrasonic method. Poly(o-aminophenol) electrodeposited on the cleaned graphite disk electrode by pulse potential electrodeposition technique from an aqueous solution containing 0.02M o-aminophenol, 0.04M sodium dodecyl sulfate, and 0.6 M perchloric acid with the pulse current of 8 mA/cm^2, pulse time and relaxation time of 0.5 s. At the start of work, the worker electrode was polished and then rinsed with ethanol and water, respectively. The MnO_2-poly (o-aminophenol) electrode was prepared like the method of graphite, poly(o-aminophenol) electrode, but with an addition of 1% MnO_2. The MnO_2 1% were scattered into a solution of 5 mM SDS for thirty minutes to acquire a uniform suspension. Sodium dodecyl sulfate is used as suspension additive MnO_2 particles and increase the firmness and electroactivity of the prepared films.

3. Results and Discussion

Figure 1 exhibits the SEM images of poly(o-aminophenol) and MnO_2-poly(o-aminophenol). As can be observed, the morphologies of poly(o-aminophenol) and MnO_2-poly(o-aminophenol) are completely different from each other, indicating that the presence of MnO_2 into poly(o-aminophenol)

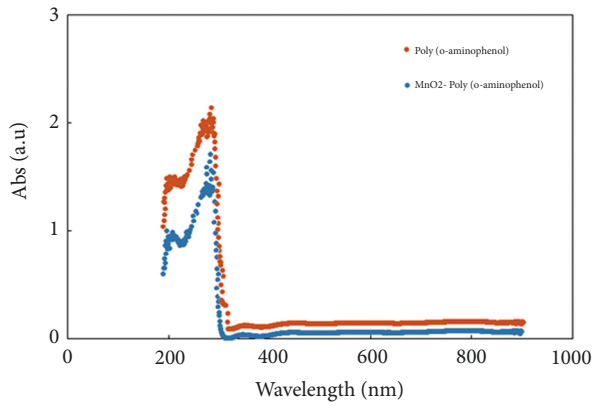


Figure 2: UV-Vis absorption spectrum of the poly(o-aminophenol) and the MnO_2-poly(o-aminophenol) nanocomposite.

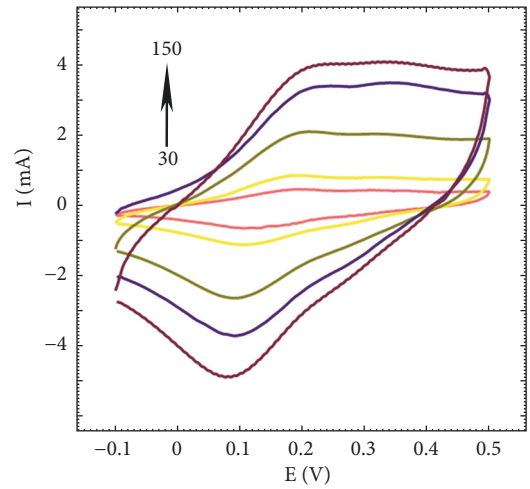


Figure 3: CV curves of the G/MnO_2-poly(o-aminophenol) electrode obtained in 1mM $K_3Fe(CN)_6$ solution containing 0.5 M KCl at different scan rates (30, 60, 90, 120, 150 mv^{-1}).

changes the microstructure of the polymer. The SEM image of the POAP coating has slightly porous structure; however, the use of MnO_2 nanoparticles seems to make the coating porous and more compact than pure polymer that present large specific surface. The micrograph shows that the POAP thin films deposited in the presence of MnO2 are very thick and present a smooth surface. Since the MnO_2 particles, alone have a more porous structure. It should be noted that the electrochemical polymerization process does not change the morphology of MnO_2 seeds, but the particle coating with POAP coating reduces the surface roughness of the particles. It is clearly seen that the surface morphology of the polymer significantly altered by adding MnO_2 nanoparticles. As is clear, MnO_2 particles are uniformly doped throughout the polymer. The distribution of MnO_2 particles in the polymer structure is well known.

Figure 2 displays UV-Vis spectrum prepared films of the poly(o-aminophenol) and MnO_2-poly(o-aminophenol). It is observed that the shapes of UV spectra of nanocomposite and polymer are similar, but the poly(o-aminophenol) sample showed strong absorption band in the UV region. As observed by adding MnO_2, the severity of the peaks decreased because of the interaction between MnO_2 and poly(o-aminophenol), demonstrating of the MnO_2 presence in the composite film. When MnO_2 nanoparticles are dispersed in the polymer matrix, significant changes are observed in the absorption spectra, which indicate the interaction of metal-oxide nanoparticles with the polymeric chain. These results confirm the formation of MnO_2-poly(o-aminophenol) nanocomposite.

The surface areas of the bare and modified electrode were gained by cyclic voltammetry method in 1 mM $K_3Fe(CN)_6$ solution as a probe at various scan rates. The surface area for a reversible process can be computed according to the slope of as (1) [23]:

$$i_p = 2.69 \times 10^5 An^{3/2} D^{1/2} c\nu^{1/2} \quad (1)$$

where A is the electroactive surface area (cm^{-2}), while n is the amount of electrons participated in the redox reaction. D, C, ν are the diffusion coefficient ($cm^2\ s^{-1}$), bulk concentration of the redox probe (mol cm^{-3}), and scan rate (Vs^{-1}), respectively. For a solution containing K_3 $Fe(CN)_6$, the surface areas of the graphite, G/poly(o-aminophenol), and G/MnO_2-poly(o-aminophenol) electrodes were computed 0.071, 0.265, and 0.326 cm^2, respectively. The relative standard deviation (RSD %) for three determinations is 2.1% for the graphite, 2.7% for the G/poly(o-aminophenol), and 3.2% for the G/MnO_2-poly(o-aminophenol) electrodes, indicating the good repeatability of electrodes.

Figure 3 illustrates the curves of the G/MnO2-poly(o-aminophenol) (c) electrodes obtained in 1 mM $K_3Fe(CN)_6$ solution containing 0.5 M KCl at various scan rates. As shown in the figure, two distinct peaks are seen for electrode. This shows the MnO_2-poly(o-aminophenol) has higher electrochemical activity and has very low variations in peak and potential difference ΔEp. large peak potential represents the porous structure and larger specific surface area.

It is obvious that the redox peak current growths linearly with enhance scan rate and the redox peak currents of G/MnO_2-poly(o-aminophenol) significantly was strong. Figure 4 shows a linear dependence of anodic current for G/MnO_2-poly(o-aminophenol) electrode on the $\nu^{1/2}$ with a correlation coefficient of 0.9909.

Figure 5 shows cyclic voltammogram cycles of the bare and obtained electrodes (pure poly (o-aminophenol), MnO_2-poly(o-aminophenol)). As seen, the pure poly(o-aminophenol) film shows a pair of the wide peak of about -0.1 to +0.5 V, which is associate to the redox reaction of the phenoxazine. The redox peak currents of the composite film were stronger than both electrodes. The composite shows a higher background current in the potential sweep, and there exists faradic currents, because of the existence of MnO_2.

Figure 6 shows CV curves of G/poly(o-aminophenol) and G/MnO_2-poly(o-aminophenol) electrodes have been depicted in different scan rates in 0.6 M HClO4 media. As seen, two pairs of peaks become visible on the chart in CV of

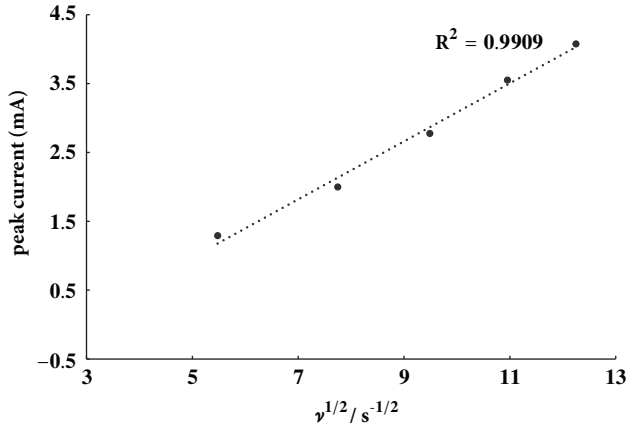


Figure 4: Peak currents as a function of $\nu^{1/2}$ of G/MnO2-poly(o-aminophenol) electrode.

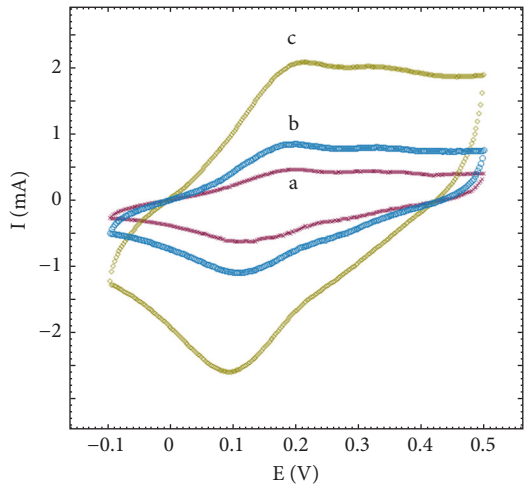


Figure 5: Cyclic voltammograms of (a) bare, (b) poly(o-aminophenol), and (c) MnO_2-poly(o-aminophenol) electrodes obtained in 0.6 M HClO4 solution at the scan rate of 50 mVs^{-1}.

both electrodes. Based on CV results, with increasing scan rates, the current response of both films increases, but the current signal is low in G/poly(o-aminophenol). Clearly, with the increase in scan rate gradually, the shape of cyclic voltammograms does not deform strongly. It is clear that, the change at the peak potential of MnO_2-poly(o-aminophenol) film is smaller than that for poly(o-aminophenol). These results confirm that it has a better electrochemical reversibility and an ideal capacity compared to poly(o-aminophenol).

Figure 7 shows the I–V characteristics of bare, MnO_2-poly(o-aminophenol) composite, and poly(o-aminophenol) electrodes [24]. The specimen resistance was measured using two-probe, where the I–V curves were obtained by scanning the voltage from -2 to 2 V with a step of 0.06 V. I–V curves display that the resistance of MnO_2-poly(o-aminophenol) composite has decreased compared to poly(o-aminophenol) and bare electrodes. These data show the electro-catalytic effects of MnO_2-POAP towards oxygen evolution reaction (OER) and hydrogen evolution reaction (HER), in comparison to pristine POAP.

The ability of electron transfer of different electrodes was studied by using electrochemical impedance spectroscopy at the open-circuit potential for investigation of a polymer matrix. Figure 8 shows the Nyquist impedance curve of the electrodes using a 1 mM redox $[Fe(CN)_6]^{-3/-4}$ (1:1) probe with 0.5 M KCl solution. It shows that both electrodes exhibit a single semicircle at higher frequency region and a linear part in the lower frequency region. As predicted, the electron transfer (Ret), which is related to the faradic reactions in the MnO_2-poly(o-aminophenol) electrode, is less than pure polymer. This result shows that the presence of MnO_2 nanoparticles in the polymer matrix increases the conductivity of the composite electrode. It causes charge-transfer resistance decrease with MnO_2 nanoparticles. This phenomenon may be attributed to the large specific surface and faster transfer of composite electrons. It is clear that the vertical curve of MnO_2-poly(o-aminophenol) has the large slope that is close to the imaginary impedance axis. It shows MnO_2-poly(o-aminophenol) has the high conductivity or low internal resistance. This means that the results of both experiments consist of the impedance and cyclic voltammetry tests confirm each other. As shown in the diagram, both electrodes have Warburg (ZW) resistance impedance in the low-frequency region, is a result of the dependence of the ion emission/transfer frequency from an electrolyte to the electrode surface [25]. The Nyquist design data is placed in an equivalent circuit, shown in Figure 8, indicating the a bulk solution resistance Rs, a charge-transfer resistance R ct, a constant phase element for simulating the double-layer capacitance (Cdl), and a Warburg (ZW) resistance impedance.

Considering the higher voltages in the cyclic voltammogram of MnO_2-poly(o-aminophenol), a larger capacity for MnO_2-poly(o-aminophenol) is predictable, and the MnO_2-poly(o-aminophenol) composite acts as a supercapacitor with a high specific capacitance. The specific capacitance of the samples can be estimated from the cyclic voltammetry curves based on this equation [26]:

$$\mathbf{C_{sp}} = \frac{\mathbf{i}}{\mathbf{s} \times \mathbf{m}} \tag{2}$$

which is in this equation I identify the average cathodic current, s specifies the applied potential sweep rate, and m is the mass of the active electrode. An electrode is weighing, before and after the deposition process, which yields the amount of the active material or mass of film. The specific capacitance values of the pure poly(o-aminophenol) and MnO_2-poly(o-aminophenol) nanocomposite samples are calculated as 335, and 645 F/g, respectively. The enhanced electrochemical performance of the ternary MnO_2-poly(o-aminophenol) nanocomposite electrode originates from the combined effects of the poly(o-aminophenol) and MnO_2 components.

Table 1 shows comparison of specific capacitances for different composites. Considering no reports regarding MnO_2-poly(o-aminophenol) nanocomposite, it is observed that

Table 1: Comparison of specific capacitances for different composites.

composite	Specific capacitance/Fg^{-1}	References
polypyrrole/MnO2	**141.6**	**[14]**
POAP/Dy_2O_3	**145**	**[15]**
poly-o-phenylenediamine/ MnO_2	**262.2**	**[17]**
poly(p-styrenesulfonate) grafted reduced grapheme oxide/polyaniline/MnO_2	**425**	**[27]**
poly-aniline/ MnO_2	**210**	**[28]**
This work	**645**	**-**

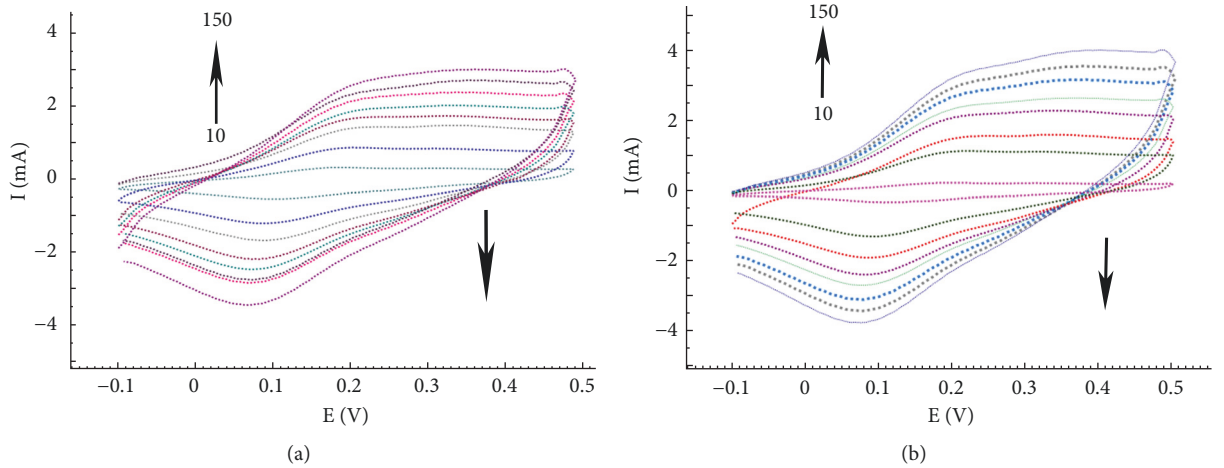


Figure 6: Cyclic voltammograms of G/poly(o-aminophenol) (a) and G/MnO_2-poly(o-aminophenol) (b) in 0.6 M HClO4 solution at different scan rates 10, 30, 50, 70, 90, 110, 130, and 150 mV s^{-1}.

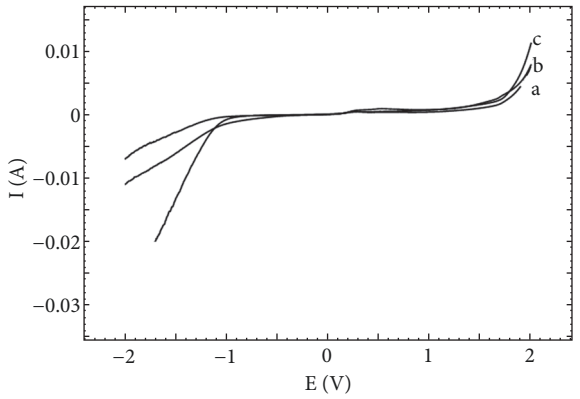


Figure 7: I–V characteristics of (a) bare electrode, (b) poly(o-aminophenol), and (c) MnO_2-poly (o-aminophenol).

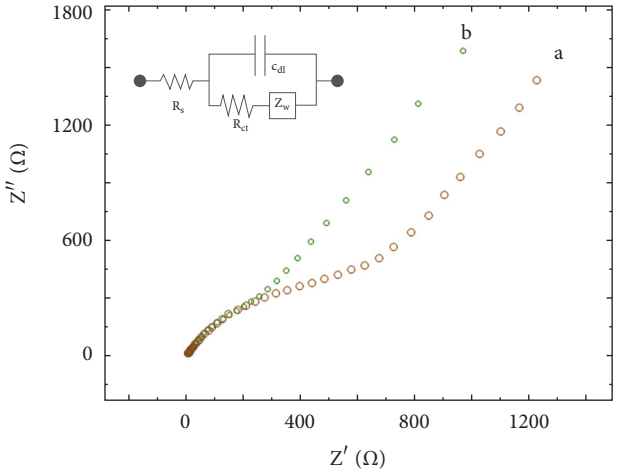


Figure 8: Nyquist diagrams of (a) poly(o-aminophenol) and (b) MnO_2-poly(o-aminophenol) films in 1mM redox probe $[Fe(CN)_6]^{-3/-4}$ (1:1) with 0.5 M KCl solution.

the MnO_2-poly(o-aminophenol) nanocomposite has a better specific capacitances.

4. Conclusions

In summary, G/MnO_2-poly(o-aminophenol) electrode was made by electropolymerization of ortho-aminophenol monomer and of MnO_2. Optimum conditions for the providing of modified electrode have been obtained. With the presentation of MnO_2, the as-prepared MnO_2-poly(o-aminophenol) exhibits more capacitive behaviors than poly(o-aminophenol), especially at the high potential scan rate. In addition, the cyclic performance of the MnO_2-poly(o-aminophenol) electrode is superior to poly(o-aminophenol). Better electrochemical capacitor property was observed for these metal-oxide polymer composites

against pure polymer. In addition, the results revealed that the MnO_2/poly(o-aminophenol) had higher electric conductivity, less resistance, and faster charge-transfer than the pure polymer film. Scanning electron micrographs and UV-Vis spectrum were employed for characterization of the produced composites. The composite represented excellent electrochemical capacitor property.

Data Availability

All of the data used to support the findings of this study are included in the article.

Conflicts of Interest

The author declares that they have no conflicts of interest.

Acknowledgments

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