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Synthesis and Electrochemical Characterization of Iron Oxide / Activated Carbon Composite Electrode for Symmetrical Supercapacitor

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***Abstract*—**In the present work, we have developed a symmetric electrochemical capacitor based on the nanostructured iron oxide (Fe_3O_4)-activated carbon (AC) nanocomposite materials. The physical properties of the nanocomposites were characterized by Scanning Electron Microscopy (SEM) and Brunauer-Emmett-Teller (BET) analysis. The electrochemical performances of the composite electrode in 1.0 M Na_2SO_3 and 1.0 M Na_2SO_4 aqueous solutions were evaluated using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The composite electrode with 4 wt% of iron oxide nanomaterials exhibits the highest capacitance of 86 F/g. The experimental results clearly indicate that the incorporation of iron oxide nanomaterials at low concentration to the composite can improve the capacitive performance, mainly attributed to the contribution of the pseudocapacitance charge storage mechanism and the enhancement on the effective surface area of the electrode. Nevertheless, there is an optimum threshold on the amount of iron oxide that needs to be incorporated into the composite system. When this optimum threshold is exceeded, the capacitive performance of the electrode starts to deteriorate, as a result of the undesired particle aggregation, which is clearly indicated in the SEM analysis. The electrochemical performance of the composite electrode is found to be superior when Na_2SO_3 is used as the electrolyte, if compared to the Na_2SO_4 solution. It is believed that Fe_3O_4 nanoparticles can provide favourable surface adsorption sites for sulphite (SO_3^{2-}) anions which act as catalysts for subsequent redox and intercalation reactions.

***Keywords*—**Metal oxide nanomaterials, Electrochemical Capacitor, Double Layer Capacitance, Pseduocapacitance.

I. Introduction

THE environmental concern on the conventional production of energy from fossil fuel has led to the establishment of several renewable alternatives [1]. Renewable resources such as the sun, ocean tides and wind are considered to be the most appropriate resources for the replacement of the fossil technology towards the production of clean and sustainable energy for consumption. Nevertheless, man has limited control over natural phenomena due to the climate/geographical constraints. Thus most of the energies that are generated during the optimum operation period may not coincide with the peak consumption period. In addition, the requirement of energy for certain remote applications also cannot be fulfilled by such renewable resources, mostly attributed to the distance and carrier constraint. For these reasons, energy storage technology appears as one of the most promising options in tackling such problems since renewably-generated electrical energy can be stored during the optimum period for future use.

Electrochemical capacitor, also known as supercapacitor, has received considerable research interest in energy storage development, mainly attributed to its unique capacitive properties, such as fast energy delivery, reasonable short charging period, attractive specific power, long durability as well as environment-friendly features [2]. The charge storage mechanism of the electrochemical capacitor is found to be distinctively different if compared to the conventional electrostatic capacitor. Electrochemical capacitor stores its charge via double layer concept in which charges are accumulated on the interfaces between the electrode and electrolyte. This is called electrochemical double layer capacitance (EDLC) and is a common phenomenon that is encountered in some porous and high surface area material, such as carbonaceous compound. By incorporation of some metal oxide nanomaterials into the carbon compound, additional pseudocapacitance effect can be observed and this overall shall improve the electrochemical performance of the electrode. Pseudocapacitance arises from the Faradaic redox process, involving the participation of some functional groups in the oxidation / reduction process, which can enhance the ionic conductivity and thus the charge storage capability [3].

The charge storage mechanism of electrochemical capacitor is found strongly depending on the types of the core electrode used. Generally, electrode materials that with intriguing capacitive property generally can be classified into three major categories, namely carbonaceous compound (activated carbon, CNT, graphene, carbon aerogel), transition metal oxides (RuO_2, NiO_2, MnO_2, Fe_3O_4) and conducting polymers (polypyrrole, polyaniline, polythiophene) [4]-[6]. The charge storage

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capability of the carbonaceous compound normally is associated with the double layer storage mechanism, which the accumulation of the charge is occurred within the porous structure and on the surface of the core electrode materials. There is no charge transfer occurred across the surface of the electrode. Due to this reason, this kind of charge transfer process does not involves any Faradaic reaction and therefore the carbonaceous materials always are classified as the core electrode compound for electrochemical double layer capacitor (EDLC) [7]. On the other hand, the charge storage mechanism for metal oxide nanomaterials and conducting polymers are always involving redox process. The Faradaic reaction between the core electrode compound and electrolyte ions within an appropriate given voltage window gives rise of pseudo-capacitance, as result of electron transfer via various oxidation state changes, in complement to the Faraday's laws [8].

In recent years, there are plenty of efforts has been devoted to the synthesis of nanostructured transitional metal oxides materials to be used as the effective core electrode compound [9]–[11]. Ruthenium dioxide (RuO_2) for example has been studied comprehensively, mainly attributed to its unique conductive behavior, apart from its intriguing three different distinct oxidation states. RuO_2 nanomaterials exhibit interesting pseudo-capacitive behaviors in acidic solutions and has been explored extensively for more than 30 years [12]. Even though ruthenium dioxide nanomaterial is found to have reasonably high specific capacitance, its potential application is still limited and hindered by its relatively high fabrication cost [13]. As such, it is imperative to continue the research for novel high performance pseudocapacitive material with reasonably fabrication cost, in order to support the continuous growing demand for manufacturing quality and cost-effective supercapacitor, in line with the steep advancement of consumer electronic products and technology. There are substantive research efforts to explore the potential of several other transition metal oxide nanostructured materials, with various unique oxidation states, such as NiO [14]–[17], MnO_2 [18]–[20], SnO_2 [21]–[23], Fe_2O_3 [24]–[26] and Fe_3O_4 [27]–[29], which show potential as effective substitutes for RuO_2 nanomaterials.

In the current work, we have attempted to adopt nanostructured Fe_3O_4/AC composite to be used as the core electrode materials. The nanocomposite material is prepared via simple facile mechanical mixing in dispersive solvent, followed by intercalation of appropriate aqueous electrolyte. The problem associated with the commonly reported poor electric conductivity of Fe_3O_4 is overcome by the incorporation of a predetermined amount of carbon black into the system, which is found can enhance the electrochemical performance of the Fe_3O_4 composite electrodes significantly.

II. Experimental Methodology

A. Preparation of the Composite Electrodes

The core electrode materials were prepared by doping different amount of iron oxide (Fe_3O_4) nanomaterial (Sigma Aldrich, particle size <50nm, BET surface ~ $38 m^2g^{-1}$) to activated carbon (AC) (Sigma Aldrich, BET surface ~ 900 m^2g^{-1}) to form the composite electrodes, containing carbon black powder (Ketjenblack, EC-600JD from Akzo Nobel, surface area ~ $1400 m^2/g$) as the conductive element and polytetrafluoroethylene (PTFE) as the polymer binder, in the weight proportion of 80:15:5. The mixture was dissolved in a mixed solvent of distilled water and isopropanol, at the weight ratio of 1:1. An amount of 15 wt% carbon black was found able to enhance the electrode conductivity of Fe_3O_4 nanomaterial significantly [13]. After a constant force of stirring, the mixtures transformed into dough form and then were cold rolled into 8 mm thick films. The composite films were then punched into coin-shaped of $2cm^2$ and were subjected for drying at 80°C for 45mins, in order to evaporate the isopropanol solvent completely. The dried composite electrodes were immersed overnight in 1M Na_2SO_3 and 1M Na_2SO_4 electrolyte respectively. The composite films were then mounted onto a stainless steel-current collector within a Teflon cell via screw-fitting plug method before the electrochemical measurements were conducted.

C. Instrumental Characterization

The surface morphology of the composite was studied by a field-emission scanning electron microscope (FESEM, FEI, Quanta 400 F). Five-point surface area and pore size measurement were performed using a Micromeritic, ASAP 2020 Brunauer-Emmett-Teller (BET) analyzer, under constant purging of N_2 gas. Electrochemical analysis, such as cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were conducted using Autolab potentiostat (model: PGSTAT128N), which is equipped with Nova analytical software. The specific capacitances (C_s) of the composite electrode were determined by using half integrated area of CV curves using the following equation: $C_s = Q/m \Delta V$, where Q is the charge, m is the mass of the electrode and ΔV is the width of the potential window.

III. Results and Discussions

A. Scanning Electron Micrograph (SEM)

The scanning electron micrographs of the composite electrode are illustrated in Fig. 1. The micrographs reveal that the content of iron oxide nanoparticles loaded onto the composite electrodes affect the surface roughness. The higher of Fe_3O_4 loading, the composite materials seem to be more compact and exhibit smoother surface topology. These findings seem to be in complement with the observations from another research study by Kim et al. [9], which they found that increasing the amount of ruthenium dioxide compound in the composite system would decrease the surface roughness of the

electrodes and thus subsequently affect the specific capacitance performance. The SEM images also show that pitted and fragmented surfaces are more prominent for the pure AC and 4 wt% Fe_3O_4 composite electrodes while the relatively compact and rigid surface structures are observed for samples with higher Fe_3O_4 nanomaterials loading. The compact surface contour will restrict the diffusion of the electrolyte ions into the porous network of the AC electrode, resulting in the loss of overall capacitance of the composite electrodes.

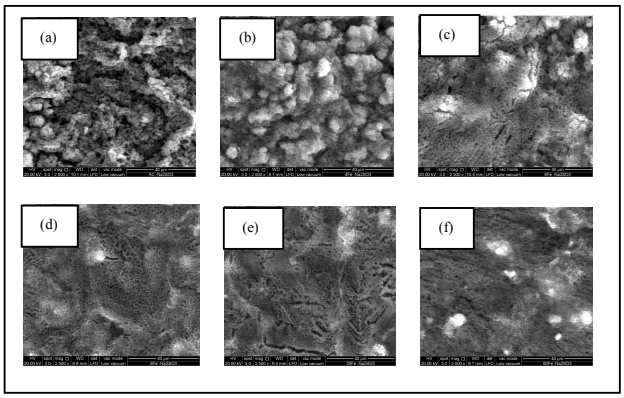

Fig. 1 Scanning electron micrographs (SEM) of the composite electrodes with different Fe_3O_4 loading: (a) AC, (b) 4 wt% Fe_3O_4, (c) 6 wt% Fe_3O_4, (d) 8 wt% Fe_3O_4, (e) 20 wt% Fe_3O_4, (f) 60 wt% Fe_3O_4

B. BET Analysis

The surface area and porosity properties of the composite electrodes are evaluated using BET analysis and the summarized results are presented in Table I. The BET analysis reveals that by loading 4wt% of Fe_3O_4 into AC, the specific surface area of composite material can be significantly enhanced from 916 to 949m^2g^{-1} and therefore improves the capacitive performance of the composite electrode effectively. This observation is in good accordance to the research finding by Zhang and Chen (2008), which clearly indicate that the enhanced capacitance is attributed to the high surface area of the core electrode material [4].

TABLE I
THE BET SURFACE AREA OF Fe_3O_4-AC NANOCOMPOSITE ELECTRODES

Electrode Material	BET Surface Area (m^2/g)
AC	916.00
4 wt % Fe_3O_4/AC/CB	949.03
8 wt % Fe_3O_4/AC/CB	831.76
60 wt% Fe_3O_4/AC/CB	800.73
Fe_3O_4	38.41

On the other hand, it is found that by further increase of Fe_3O_4 compound to 60 wt%, the specific surface area of the composite electrode starts to be distorted and the value decreased to 800m^2g^{-1}, which is a remarkable15.7% surface area reduction. At high concentration, iron oxide nanoparticles are believed starting to aggoloromerate within composite electrodes, as being observed in the SEM image (Fig. 1 (f)). The coalescence of the Fe_3O_4 nanoparticles can reduce electrolyte ionic migration, and subsequently causes the increase in diffusion path length. As a result, the capacitive performance will be distorted and similar observations have been reported in other literature as well [9], [10].

C. Electrochemical Characterization

The CV plots for the Fe_3O_4/AC nanocomposite electrodes in 1M Na_2SO_3 and 1M Na_2SO_4 electrolytes are illustrated in Figs. 2 and 3, respectively. The analysis is conducted at a constant scan rate of 10mV s^{-1}. It is worth to note that the characteristics symmetrical CV curves of EDLC are generally not being observed, especially in Na_2SO_3 solution. The deviation of the samples from exhibiting the perfect rectangular voltammograms is believed arise from the substantial contribution of pseudocapacitance contribution to the system.

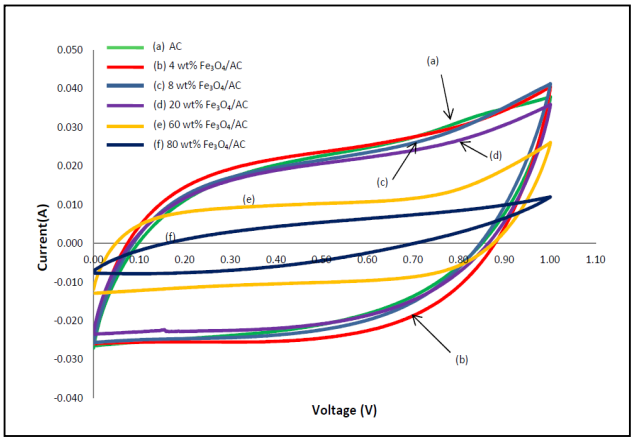

Fig. 2 Cyclic voltammograms for AC electrodes with different Fe_3O_4 nanomaterials loading in 1M of Na_2SO_3

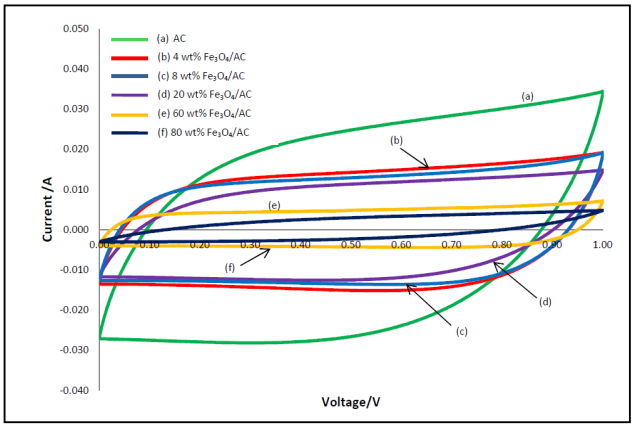

Fig. 3 Cyclic voltammograms for AC electrodes with different Fe_3O_4 nanomaterials loading in 1M of Na_2SO_4

From the voltammograms, it can be clearly observed that the current response of the 4 wt %Fe_3O_4 electrodes in 1M Na_2SO_3 electrolyte is greater than the AC and other composite electrodes, implies the most superior capacitive performance is achieved for such composition. The superior performance of the

composite electrode in Na_2SO_3 electrolyte solution is believed originated from the presence of Fe_3O_4 nanoparticles, which the nanomaterials can provide favorable surface adsorption sites for sulphite anions that act as catalysts to induce subsequent redox and intercalation reactions.

It is interesting to note that the types of electrolyte are playing essential roles to affect the CV performance of the electrode. It is apparent that the capacitive performance of the electrode in Na_2SO_4 solution is found to be distinctly different if compared to Na_2SO_3 electrolyte. In fact, the composite electrode is found to exhibit better specific capacitance in Na_2SO_3 electrolyte if compared to Na_2SO_4 solution. An implication of these results suggests that the Fe_3O_4 loaded AC composite electrodes can have different charge storage mechanisms in both sulphite and sulphate electrolytes.

Nevertheless, a further increase in Fe_3O_4 content within the range 20 – 60 wt % starts deteriorating the capacitive behaviour of the composite electrodes. The decrease in specific capacitance is attributed to the low conductivity of Fe_3O_4 nanoparticles in large amount, which in turn increase the equivalent series resistance (ESR) of the electrode. The specific capacitances of pure Fe_3O_4 electrodes generally are very low, which clearly dictates its poor charge storage capability. These results are found to be well corroborated with the similar effort by Wu et al. [27]. They reported that Fe_3O_4 nanomaterial generally has a very poor conductivity and it is essential to combine the metal oxide nanomaterials with some conductive additives, in order to improve its capacitive performance.

In addition to the low conductivity of Fe_3O_4, the poor capacitive performance for the composite electrodes with high Fe_3O_4 nanomaterials loading is due to the particle agglomeration, as shown in the SEM analysis in Fig. 1. This observation is similar to another investigation that adopting hydrous RuO_2-AC as the composite electrode, which a significant distortion on the capacitive behavior is observed when the electrode is consisted of more than 40 wt % RuO_2 nanomaterials [9]. Since ion diffusion is one of the most crucial processes that control the redox reactions within the electrode material, the diffusive capability of the electrolyte ions will decrease with the increasing of the particle size. Under such circumstances, the ions thus generally require longer time to reach the entire electrodes. In addition, the agglomeration of the iron oxide nanomaterials will reduce the porosity of the electrode material, which in turn distorts the effective surface area that is available for the Faradaic process. Similar trend has been reported by Dubal et al. [30] for the Fe doped MnO_2 composite electrode that were prepared via galvanostatically deposition. The low porosity of composite electrodes at high iron oxide nanomaterials loading can lead to the agglomerations and subsequently block most of the pores within the surface network, preventing the electrolyte ions to diffuse into the inner parts of the porous network.

D. Electrochemical Impedance Spectroscopy

In order to gain insight on the intrinsic electrochemical properties of the AC and composite electrode, EIS measurement was carried out within the probed frequency range of 10^4 to 10^{-2} Hz. Fig. 4 illustrates the Nyquist plots of AC impedance of the composite electrodes with different Fe_3O_4 loadings, by adopting Na_2SO_3 solution as the electrolyte. It can be clearly observed that the impedance curve consists of an arc and followed by a slanted line at low frequency. While in the high frequency region, the intercept of the semicircle on the real axis of the Nyquist spectrum represents the solution resistance (R_{sol}) which can be correlated to the ohmic resistance of the electrolye in the system.

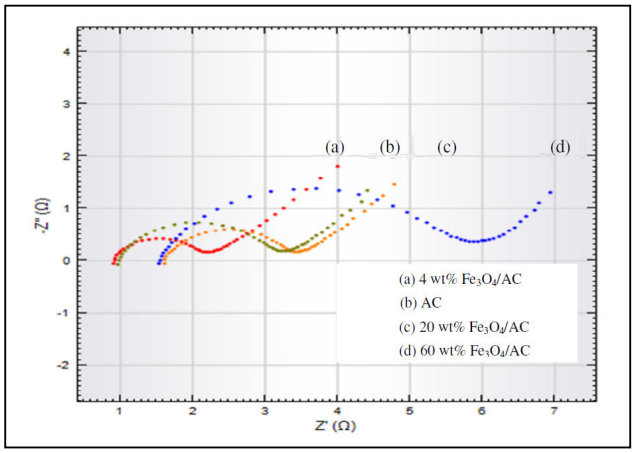

Fig. 4 Nyquist plots obtained for composite electrodes with different Fe_3O_4 loading, within the frequency range of 100 kHz – 100 mHz in 1 M Na_2SO_3 solution

The semicircles in the high- and mid-frequency regions are attributed to the charge transfer resistance between the interfaces of the electrode materials and electrolyte. The electron transfer which occurs in these regions during the charge/discharge processes is conceptualized by an interfacial charge transfer resistance (R_{ct}) or polarization resistance (R_p). Beyond the semicircle region, the Nyquist spectrum shows a long tail in the low-frequency region, which can be associated to the Warburg resistance of the electrode. As dictated in Fig. 4, it is apparent that the sizes (diameter) of the Nyquist semicircles are varied for the electrodes with different Fe_3O_4 loadings. When Na_2SO_3 is used as an electrolyte, the R_{ct} for the electrodes is found to decrease in the order of 4.28 Ω (60 wt %), 1.87 Ω (20 wt %) and 1.37 Ω (4 wt %), implying the relatively low internal resistivity for the electrode that is loaded with small amount of iron oxide nanomaterials.

From these results, it is apparent that the composite electrode consists of 4 wt % Fe_3O_4 /AC active material exhibits the lowest R_{ct} value, consistent with the smallest size (diameter) of the Nyquist semicircle within the high frequency region. A reduction in the value of R_{ct} implies that the surface modification by addition of fairly small amount of iron oxide nanomaterials can actually improve the conductivity of the composite electrode and thus enhances its capacitive performance, which is in accordance to the results obtained from CV measurement.

IV. Conclusion

In this study, the electrochemical capacitive performance of iron oxide-activated carbon nanocomposite electrode materials has been evaluated. Two different electrolytes (Na_2SO_3 and Na_2SO_4) are adopted in the system. It is found that the bulk increasing of the iron oxide nanomaterials content can distort the capacitive performance and deteriorate the specific surface area of the electrode, mainly attributed to the aggregation of the Fe_3O_4 particles within the composite. In addition, the composite electrode that utilizes Na_2SO_3 electrolyte is found to have a superior charge storage performance if compared to the Na_2SO_4 solution. It is believed that iron oxide nanomaterials can provide favorable surface adsorption sites for sulphite (SO_3^{2-}) anions during the Faradaic and intercalation reactions. The enhancement of the capacitive performance for the composite electrode is believed originated from the synergistic effect of double layers and pseudocapacitance charge storage mechanism, apart from the specific surface area enhancement of the core electrode materials.

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