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The Potential of BiPO4 as Electrode Material and its Electrochemical Performance on AC-Mn2O3-BiPO4 Film Electrode

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Abstract. . Supercapacitors as one of the energy storage have attracted attention. The advantages of using carbon materials have so far been widely developed and researched as electrodes for supercapacitors, but their volumetric capacity is still less than optimal and less practical in long-term use. Manganese (III) oxide (Mn2O3) materials show great potential as electrodes with high theoretical specific capacitance. On the other hand, BiPO4 as an anode has added battery characteristics to get maximum results. The blending method is applied in the manufacture of composites deposited on an aluminum foil substrate. The electrochemical properties of the developed samples were studied by cyclic voltammetry (CV), Galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS). The electrochemical results showed that the best electrode-specific capacitance at 20% BiPO4 percentage reached 56 Fg-1 at a current density of 1 Ag-1 with a potential window of 2 V for 50 cycles. It is hoped that these results can provide information on the potential of using the material as an optimal electrode.

1 Introduction

Technological developments are one of the factors that influence the continued increase in energy demand with the limited energy sources available on Earth. The utilization of renewable energy such as biomass and solar cells is an effort to overcome energy limitations. Supercapacitors are one example of an efficient and effective energy storage technology that must be developed. One of the most effective and efficient forms of energy storage is a supercapacitor (EDLC). Generally speaking, EDLC is made up of three primary parts: electrodes, electrolytes, and separators [1]. Supercapacitors have attracted the interest of industry and academia due to their distinctive characteristics features including high power density, quick charge-discharge rates, and good stability [2]–[5].

Numerous electrode materials for energy storage combining faradic reactions and electrostatic attraction have been studied in an effort to improve the electrochemical characteristics of capacitors. Many carbon-based composites have been developed, such as polymer/carbon and metal oxide/carbon composites. Increasing the energy density becomes one of the important things to obtain a good energy storage device while still maintaining the specifics of the material itself. Electrochemical capacitors are called ultra-capacitors or what we hear more often with supercapacitors.

Supercapacitors are widely used as a backup energy source because charging is easy and can be obtained in a very short time. Since batteries have a higher energy and power density than supercapacitors, hybrid devices are chosen to be able to combine battery-type electrodes and supercapacitor-type electrodes. However, carbon-based supercapacitors still have a low energy density at this time [6].

Recent research developments have combined $BiPO_4$ with several materials such as carbon and metal oxide-based materials. Metal phosphate is becoming one of the new cathode materials for supercapacitors because it is non-toxic, low-cost, environmentally friendly, and abundant. In addition, good crystallinity and chemical stability, high thermal stability, and specific redox activity make $BiPO_4$ an ideal supercapacitor material. $BiPO_4$ is one of the Bismuth-based materials that has been widely developed for various applications, such as photocatalysts [7], [8], luminescent [9]sensors [10], radioactive ion separators [11] and supercapacitor energy storage devices [12].

Bi-O-P has an inductive characteristic, which initiates the use of BiPO4 as an electrode material in supercapacitor and pseudocapacitor applications, BiPO4 has a high capacitance value as a negative electrode material [13],[14].

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The combination of Mn_2O_3 (manganese dioxide) materials is capable of increasing the specific capacitance value because it has a variety of structures, low toxicity, is environmentally friendly, and has a variety of applications including catalysts, adsorption, ion exchange, good electrochemical storage. The research of activated carbon as an electrode material has a low supercapacitor energy density, this encourages further research to mix activated carbon materials with metal oxide (Mn_2O_3) and metal phosphate ($BiPO_4$) based materials. This is an attempt to get a supercapacitor that has a high specific capacitance and maximum performance.

2. Experimental

2.1 Synthesis of AC-Mn_2O_3-$BiPO_4$ composite

The mixing process of the AC- Mn_2O_3-$BiPO_4$ composite uses the blending method. Mass percentage variations 10, 15, and 20% $BiPO_4$ ¬(Sigma Aldrich, 99% purity), 10% wt conductive agent (carbon black), and 10% wt polyvinylidene fluoride (PVDF). The solution was stirred for 6 hours using a 300 rpm magnetic stirrer. Then, via the doctor blade technique, the composite solution was placed on an aluminum foil substrate and continued with the annealing process at 50 ^{0}C for 24 hours. Furthermore, the electrode was fabricated by combining the working electrode, separator, and electrolyte with a separator in polyethylene and 1 M ET_4NBF_4 as a liquid electrolyte.

2.2 Characterization

The developed sample surface morphology is illustrated by EDX Scanning Electron Microscopy (SEM) and cross-section. By using an electrochemical workstation (Neware), experiments were conducted on the arraigned chatodes' electrochemical properties using cyclic voltammetry (CV) and galvanostatic discharge (GCD). The two-electrode course of action was utilized to assess the electrochemical characteristics of the cathodes arranged through 1 M ET_4NBF_4 aqueous electrolyte solution. Assessment of CV, GCD, and EIS was performed with the use of a workstation, while the specific capacity (Cs) was assessed from the GCD assessment. The specific energy and strength density values are estimated via the GCD curve.

3. Result and Discussion

3.1 Morfology Electrode AC-Mn_2O_3-$BiPO_4$

The surface morphology of AC-Mn_2O_3-$BiPO_4$ film electrodes with mass variations of 10, 15, and 20% $BiPO_4$ was confirmed by SEM. As much as 80% of the composition of this electrode is an active material, namely activated carbon. As an active material, activated carbon has pores that can absorb electrolyte ions so that ion transfer will occur quickly [15]. The test results (Fig. 1 a-d) with a magnification of 2000x showed that the Mn_2O_3 and $BiPO_4$ nanoparticles

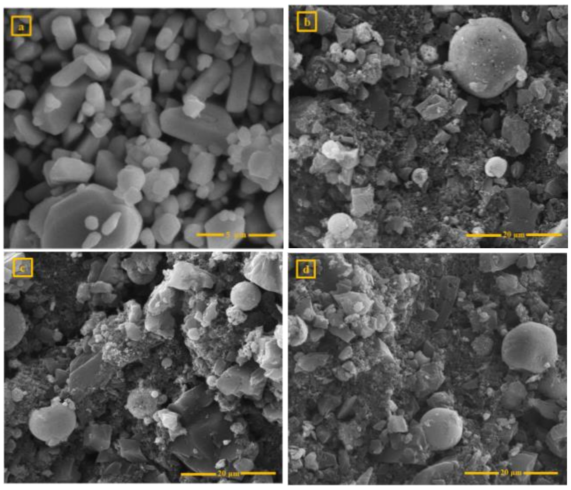


Fig. 1 Morphology of (a) $BiPO_4$ powder and film electrode variations of (b) 10%, (c) 15%, and (d) 20% $BiPO_4$

with the AC particles successfully mixed. AC particles in the form of lumps spread over the entire surface with black carbon which is also spread evenly to form a composite. Whereas the Mn_2O_3 particles look spherical in shape with the presence of $BiPO_4$ which is distributed at certain points agglomerated, but wider with increasing mass percentage of $BiPO_4$. It is evident that Mn_2O_3 particles are larger than those of AC and $BiPO_4$.

Furthermore, EDX testing was done to find out how much each element was present in the 10, 15, and 20% $BiPO_4$ variations of the AC-Mn_2O_3-$BiPO_4$ film electrodes. The test results (Fig. 2 and Table 1) show that the wt% and at% for each variation differ according to the variation in the percentage of $BiPO_4$. From the graph, it can be seen that the Bi content appears at the highest percentage, namely 20%, followed by the carbon content which also increases. This is inversely proportional to the wt% of Mn which decreases with the higher percentage of $BiPO_4$. Elements Bi and P only appear at 20% variation with P (phosphorus) content which is not too high, only around 0.22 wt% and 0.07 At%.

Table 1. EDX Results wt% of AC-Mn_2O_3-$BiPO_4$ Film Electrodes

Elements	Weight %		
	Mn-Bi 10%	**Mn-Bi 15%**	**Mn-Bi 20%**
C	32.77	31.42	42.52
O	22.12	19.05	20.64
Bi	-	-	0.22
P	-	-	0.81
Mn	41.62	43.94	26.87

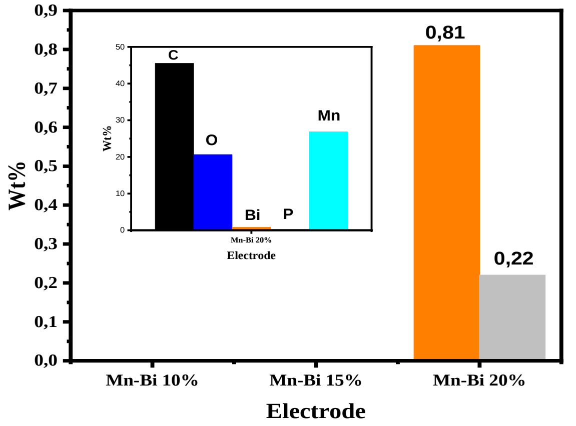


Fig. 2 Graph of EDX (wt%) film electrode AC-Mn_2O_3-$BiPO_4$

3.2 Electrochemical Performance of AC-Mn_2O_3-$BiPO_4$ Film Electrodes

The electrochemical performance of 10, 15, and 20% $BiPO_4$ AC-Mn_2O_3-$BiPO_4$ film electrodes was investigated through charge-discharge, cyclic voltammetry, and EIS characterization, respectively. The results of the cyclic voltammetry characterization (Fig. 3) were analyzed by fabricating a coin cell using a symmetrical electrode arrangement system. The voltage range used is 0-2V with a scan rate of 10 mVs^{-1} on each, and the solution of electrolytes used is 1M ET_4NBF_4. It can be seen (Fig. 3) that the addition of $BiPO_4$ mass affects the area of the CV curve formed. The AC-Mn_2O_3-$BiPO_4$ film electrode with a variation of 20% has the smallest area compared to the other two samples. This also correlates with the results of the EIS test, that at a percentage of 20%, $BiPO_4$ has a greater resistance value than the 10 and 15% variations. From the CV curve, it can be seen that the AC-Mn_2O_3-$BiPO_4$ electrode has a semi-rectangular (quasi-rectangular) shape. This indicates that the AC-Mn_2O_3-$BiPO_4$ electrode belongs to the EDLC type [16].

This is also confirmed by the use of active material in the form of activated carbon with a percentage of 80%. The CV curve of the electrode also describes the faradic characteristics due to the oxidation and reduction mechanisms of the $BiPO_4$ material [17]. This is what influences the shape of the CV curve which is obtained to have a contour at the cathodic peak is seen in variations of 10 and 20% $BiPO_4$. This indicates that $BiPO_4$ has a low internal resistance, a kinetic response that is imperfected by difffusion, and excellent thoug material [18].

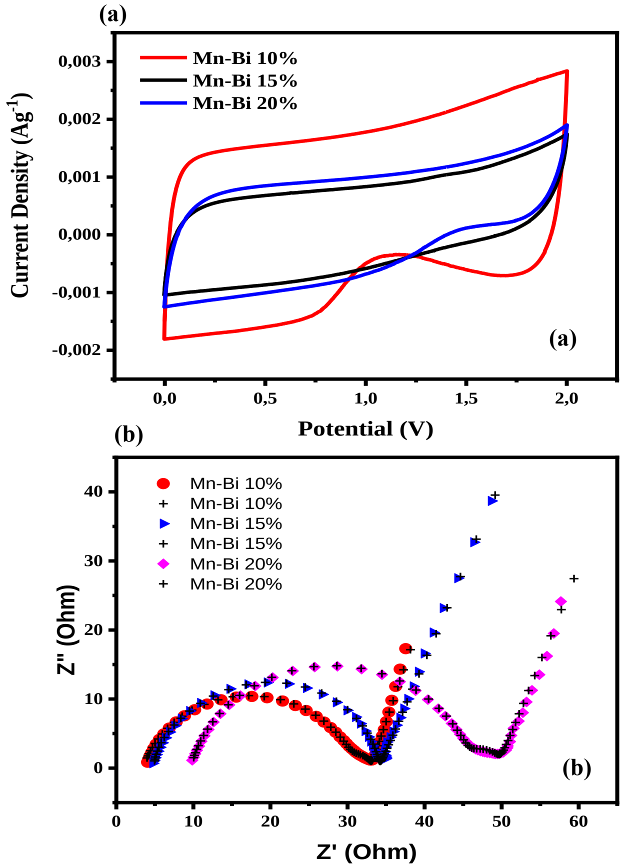


Fig.3 Curve (a) CV and (b) EIS curves of AC-Mn_2O_3-$BiPO_4$ film electrodes

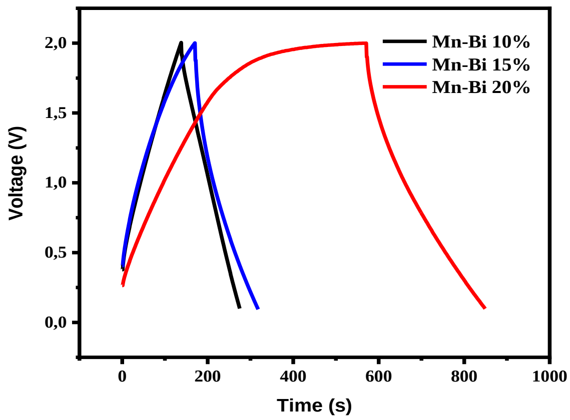


Fig. 4 Curves (a) charge-discharge of AC-Mn_2O_3-$BiPO_4$ film electrodes with variations of 10, 15, and 20% and (b) charge-discharge variations of 20% for 10 cycles

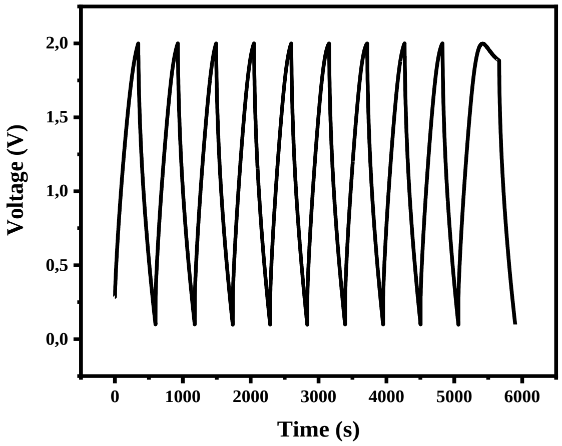
Then the specific capacitance of the AC-Mn_2O_3-$BiPO_4$ film electrode was analyzed through charge-discharge testing for each variation using Equation 1.

$$Cs = 4\,x\,\frac{I\Delta t}{m\Delta V} \qquad (1)$$

Where *Cs* is the specific capacitance (Fg^{-1}), *I* is the current (*A*) and Δt is the discharge time (*s*), and ΔV is the potential range used. Equation 1 is used to process the information from the charge-discharge graph., the specific capacitance, energy density, and power density values for each variation are produced as shown in Table 2.

Table 2 shows that the addition of $BiPO_4$ mass can increase the capacitance of the AC-Mn_2O_3-$BiPO_4$ electrode this is because Bismuth phosphate ($BiPO_4$) as a strong electrode material has high thermal and chemical stability, high theoretical capacity, and as a supporting material for supercapacitor electrodes which is supported by Mn_2O_3 material which has a high theoretical capacity value [17], [20].

The charage-discharge curve for each variation and the life cycle of the film electrode is shown in Figure 4 a-c. The curve of GCD obtained has a non-linear triangular shape with a longer time graph at 20%



(b)

BiPO$_4$ variation. The curve of GCD is also affected by a sudden drop in voltage which is called the low voltage (iR) drop. This low voltage is caused by the excess potential resulting from the reaction of the electrolyte flow and electrons at the electrodes [21]. iR drop of the charge-discharge curve indicates the internal resistance of the AC-Mn_2O_3-$BiPO_4$ electrode [22].

Table 2. Specific capacitance with $BiPO_4$ variants

Electrodes	Specific Capacitance (Fg^{-1})	Energy Density (Wh/kg)	Power Density (W/kg)
Mn-Bi 10%	30.2	13.869	363.468
Mn-Bi 10% 15%	30.8	13.508	345.950
Mn-Bi 10% 20%	56.4	24.709	355.463

As the $BiPO_4$ composition increases on the AC-Mn_2O_3-$BiPO_4$ electrode, the electrolyte ions in the space inside the electrode decrease, this causes the discharge time to decrease and the specific capacitance to decrease from the composite [22]–[24]. This also confirms the cycle stability of the AC-Mn_2O_3-$BiPO_4$ electrode. After 50 charge-discharge cycles, the 20% AC-Mn_2O_3-$BiPO_4$ supercapacitor showed a periodic decrease in charge transfer resistance.

4 Conclusion

AC-Mn_2O_3-$BiPO_4$ film electrodes have been successfully prepared with three variations of $BiPO_4$ masses. The addition of $BiPO_4$ to the AC-Mn_2O_3 electrode is proven to be able to increase the capacitance value. The highest specific capacitance value is the percentage of 20% addition of $BiPO_4$, namely 56.4 Fg-1 with energy density and power density values of 2.71 Wh/kg and 355.46 W/kg respectively. This is because, at a percentage of 20%, the value of capacitance and elapsed time is greater than the percentage of other $BiPO_4$ additions.

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