

Reduced Graphene Oxide on Activated Carbon-Manganese Dioxide Composite Materials for High-Performance Supercapacitor Electrodes

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ABSTRACT

This study presents the addition of reduced graphene oxide (rGO) on the surface of activated carbon-manganese dioxide (ACMnO₂) composite material via high-temperature variations of 350 °C to 450 °C to increase the specific capacitance of the ACMnO₂/rGO composite electrode. The composite material is synthesized by coating the slurry mixture on the aluminium sheet using a 2-step doctor blade method with polyvinylidene difluoride (PVDF) material and dimethylformamide (DMF) solution as a binder. Then symmetric supercapacitor is fabricated using filter paper as a separator and 3M potassium hydroxide (KOH) solution as an electrolyte. The composite material analysis is characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM) as well as cyclic voltammetry (CV) for the electrochemical properties. The ACMnO₂/rGO composite electrode at a temperature variation of 350 °C showed the highest specific capacitance of 459.79 F g⁻¹ at a scan rate of 9 mV s⁻¹ with an energy density of 63.859 Wh kg⁻¹. The addition of rGO on the surface of the ACMnO₂ composite material increased the specific capacitance by about 58% compared to without rGO, showing promises for high-performance supercapacitor electrodes.

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INTRODUCTION

According to Enerdata, world energy consumption has increased by 58% in the last 30 years (1990 – 2020). The top three most widely used energy sources include oil (30%), coal (26%), and natural gas (24%), of which all three are fossil fuels. The use of fossil fuels has caused negative impacts on the environment, such as the greenhouse effect and global warming, resulting in the increase of atmospheric concentration and temperature of the earth's surface by 0.85 °C between 1800 to 2012, based on assessments by the Intergovernmental Panel on Climate Change (IPCC).

The solution to these problems in the context of scientists is through research on renewable and green energy and energy storage device. However, the main problem in research on renewable and green energy is the high cost due to the massive scale of this subject. According to Europa Union, the total global investments for this research have

always exceeded USD 200 billion since 2010. Moreover, the cost of electricity from these energy sources is still much higher than fossil fuels. It makes renewable and green energy only contribute 10% of world energy consumption.

A simple definition of energy storage is a device that captures energy from various sources for conversion, which can then be reused. Supercapacitors (SCs) are a new alternative energy storage device that can combine electrochemical and electrostatic mechanisms, which result in higher specific power than rechargeable batteries and higher specific energy than conventional capacitors. SCs are particularly attractive for their superior power capabilities and outstanding cycle life but have suffered for their energy density over the past decade [1]. Therefore, the main focus of research on the SCs is finding an electrode material that can produce a high performance to satisfy the energy demand. It should have in-depth knowledge of various applications' mechanisms ranging from single devices to battery-supercapacitor hybrid devices [2].

Activated carbon (AC) is one of the carbon materials can be obtained through two processes:

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carbonization and activation from raw carbon resources. AC derived from coconut shells have advantages such as large carbon composition, high specific surface area, easily controlled pore structure, and low dust composition [3]. With ease of availability, AC from a bio-waste precursor has a specific surface area ranging from $400 \text{ m}^2 \text{ g}^{-1}$ to $3500 \text{ m}^2 \text{ g}^{-1}$ [4]. Moreover, AC performance in the supercapacitor application can be enhanced by synergistic effects with other carbon materials [5]. These effects can somehow self-support each other with their own characteristics, including structure and porosity. But electrodes from carbon material, either separate or composite, often have a specific capacitance of around 100 F g^{-1} [6].

Composite materials from AC and nano transition metal oxide become an alternative because they also provide pseudocapacitance through the redox reactions, compared to only double-layer capacitance. Manganese dioxide (MnO_2) has attracted intensive attention in the SCs because it is highly redox-active and serves fast and reversible redox reactions [7]. Furthermore, MnO_2 is highly abundant, low cost, and environmentally friendly, exhibiting a high theoretical specific capacitance (1370 F g^{-1}) and a wide potential window (1 V) compared to most other nano transition metal oxides. Its poor electrical conductivity and low active area make it suitable for loading on electrically conductive carbon materials [8]. However, combining large portions of MnO_2 with AC can damage the pore structure of AC, thereby reducing the active sites and electrolyte transfer channels [9]. Hence, it would be more appropriate to use MnO_2 in a much smaller ratio than AC. These composite materials can be synthesized by deposition methods, either solvothermal [3] or hydrothermal [10].

Reduced graphene oxide (rGO) is one of the graphene derivatives, which has various unique optical, electrical, mechanical, and thermal properties [11]. Moreover, rGO can be synthesized by a method that is considered cheaper, simpler, and more efficient than graphene. The addition of rGO to composite materials from AC and MnO_2 had previously been done but obtained a small specific capacitance of only 80 F g^{-1} because the mass percentage of 2% and the heating temperature of 100°C are not enough to facilitate rGO effectively [12]. Therefore, throughout this study, adding rGO will use a large mass percentage through a high heating temperature. As expected, it will enhance pore structure in surface morphology by ensuring rGO is on top of composite materials from AC and MnO_2 . Overall, the results showed an improvement

in electrochemical properties resulting in better supercapacitor performance than without the addition of rGO.

METHODOLOGY

Materials

AC was derived from coconut shell wastes with a specific capacitance of 80.9 F g^{-1} , a specific surface area of $1089 \text{ m}^2 \text{ g}^{-1}$, and dominant pore distribution on micropores [3]. MnO_2 (Merck) had a grain size below 30 nm. The rGO was synthesized by a modified Liquid-Phase Exfoliation (LPE) method with a heating temperature of 90°C [13]. Moreover, polyvinylidene difluoride (PVDF) material from Sigma-Aldrich and dimethylformamide (DMF) solution from Merck were also used without any modification.

Synthesis Method of Composite Materials

AC (85%), MnO_2 (5%), and PVDF (10%) materials were mixed in a beaker glass by adding the DMF solution. Then the mixture was stirred (Cimarec Digital Hot Plate Stirrer 3067-20) using 200 rpm at 80°C for 2 hours to reach a homogenous condition and slurry-like shape. Furthermore, the slurry mixture was coated on the aluminium sheet using the doctor blade method and then heated in a furnace with a temperature of 80°C for 30 minutes.

The rGO (90%) and PVDF (10%) materials were mixed in a beaker glass by adding the DMF solution. The total mass ratio between the rGO mixture and the ACMnO_2 mixture was 1:1. Then, the mixture was stirred using 200 rpm at 80°C for 1 hour to reach a homogenous condition and slurry-like shape. Furthermore, the slurry mixture was coated on the aluminium sheet containing ACMnO_2 composite materials and then heated in a furnace at various heating temperatures of 350°C , 400°C , and 450°C for 1 hour.

Fabrication Method of Supercapacitors

The components of SCs include filter paper as a separator and 3 M potassium hydroxide (KOH) solution as an electrolyte. ACMnO_2 and $\text{ACMnO}_2/\text{rGO}$ composite materials were used as electrodes with approximately $1.5 \times 1.5 \text{ cm}$ in size, 0.3 mm in thickness, and 0.005 g in mass. Then the back of the electrodes was glued to copper tape as a current collector. Symmetrical SCs were fabricated in two acrylics with screws to press all the components of SCs inside them.

Characterization Method

Specific capacitance and energy density of the SCs were measured by cyclic voltammetry (CV)

(Keithley 2400-C) measurements using data acquisition software from [14] at a voltage of 0 to 1 V with a scan rate of 9 mV s⁻¹. Both samples with rGO that have the highest specific capacitance and a sample without rGO will be further characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM)). The lattice constants and crystallite size of composite materials were obtained by XRD (Rigaku MiniFlex 600) using a copper X-rays spectrum with an angle from 10° to 80° at a rate of 0.02° min⁻¹. Distribution of the smallest size and the constituent elements, and the surface morphology of composite materials were obtained by SEM (JEOL JSM-6510 LA) on the cross-sectional images using EDX and Mapping working parameters at a voltage of 10 kV with energy ranging from 0 to 20 keV.

RESULTS AND DISCUSSION

The CV curve in Fig. 1 shows a non-square shape and a small peak at the end of the charging/discharging process because of the type of material used in the electrodes. Carbon material (AC, rGO) involves the adsorption/desorption process of ions from the electrolyte in its pores (non-faradaic), causing the CV curve to widen. Meanwhile, nano transition metal oxide (MnO₂) involves the reduction/oxidation process with the electrolyte (faradaic), causing redox peaks. Characteristics of the redox peaks in all samples did not change, indicating that the high heating temperature did not affect the crystal structure of MnO₂. However, the redox peak in the ACMnO₂/rGO-450 sample is lower than the other samples with rGO, indicating that the heating temperature above 400 °C decreased the pseudocapacitance mechanism.

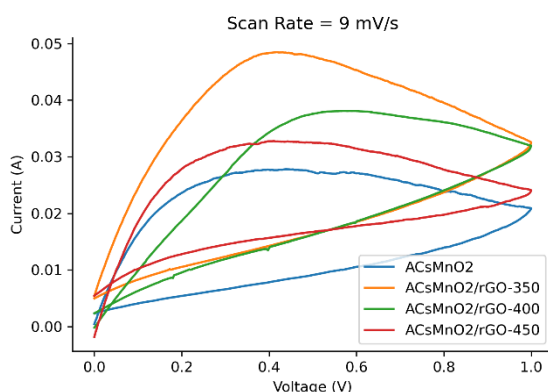


Fig. 1. The CV curve of all samples.

The rGO heating temperature is above 300 °C that resulted in the loss of water intercalation/deintercalation process, removal of more stable oxygen functional groups, and increased

ion adsorption/desorption the capacity up to 40 times [15]. However, it started to decrease when it reached a heating temperature of 500 °C. In addition, the heating temperature between 300 °C and 400 °C increased the mesopore, achieved better cycle stability, and presented a carbonyl functional group C=O [16]. In contrast to other carbonyl functional groups such as C-O-C, and O=C-O, which adversely affect the conductivity and specific surface area of rGO, C=O contributes to the pseudocapacitance mechanism.

Specific capacitance (C_s) in F g⁻¹ and energy density (E_d) in Wh kg⁻¹ are given by Eqs. (1) and (2) as follows:

$$C_s = \frac{\int i dV}{S m V} \quad (1)$$

$$E_d = \frac{1}{2} \frac{C_s V^2}{3.6} \quad (2)$$

in which $\int i dV$ (A V) is the area of the CV curve, S (mV s⁻¹) is scan rate, m (g) is the mass of the electrode materials, and V (V) is voltage. Therefore, the larger the CV curve formed, the greater the specific capacitance and energy density obtained. As shown in table 1, the ACMnO₂/rGO-350 sample has the highest specific capacitance compared to the other samples with rGO, which unexpectedly decreased specific capacitance. The addition of rGO on the ACMnO₂ sample increased the specific capacitance up to 58% compared to without rGO. Hence, the effect of high heating temperature in the addition of rGO to specific capacitance is nonlinear. However, this research cannot provide the effectiveness of the redox reaction of MnO₂ to specific capacitance or specific surface area.

Table 1. Specific capacitance and energy density of all samples

Sample	C_s (F g ⁻¹)	E_d (Wh kg ⁻¹)
ACMnO ₂	291.78	40.525
ACMnO ₂ /rGO-350	459.79	63.859
ACMnO ₂ /rGO-400	267.08	37.094
ACMnO ₂ /rGO-450	233.45	32.424

The XRD patterns in Fig. 2 fitted in using Origin 2021 software to reduce noise and assist in determining the diffraction angle and Full Width at Half Maximum (FWHM). Both XRD patterns show narrow diffraction peaks with high intensity, indicating high crystallinity of the compounds contained in the ACMnO₂ and ACMnO₂/rGO composite materials. Meanwhile, the interplanar spacing (d) between adjacent lattice planes is given by Bragg's equation as follows:

$$d = \frac{\lambda}{2 \sin \theta} \quad (3)$$

in which λ is the X-rays wavelength, and θ is the diffraction angle. The lattice constants (a , c) depend on the crystal structure, where MnO_2 has a tetragonal crystal structure while graphite has a hexagonal crystal structure. So, the lattice constants are explicitly given by Eqs. (4) and (5) as follows:

$$\text{Tetragonal} \rightarrow \frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \quad (4)$$

$$\text{Hexagonal} \rightarrow \frac{1}{d^2} = \frac{4}{3} \frac{(h^2 + k^2 + hk)}{a^2} + \frac{l^2}{c^2} \quad (5)$$

in which hkl is Miller indices from lattice planes of crystal structure.

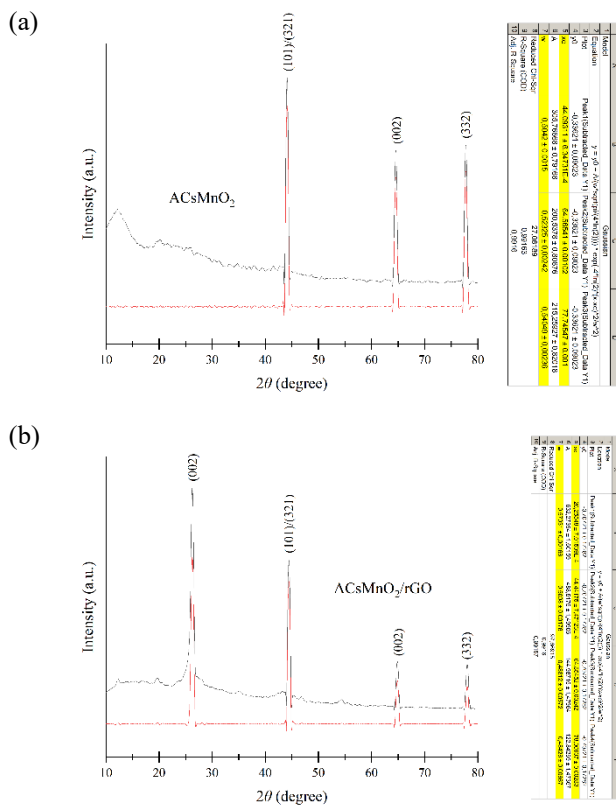


Fig. 2. The XRD pattern of (a) ACMnO_2 and (b) $\text{ACMnO}_2/\text{rGO}$ samples.

The XRD pattern of the ACMnO_2 sample in Fig. 2a shows diffraction peaks at angles of 44.093° , 64.565° , and 77.745° , corresponding to graphite (101) and $\alpha\text{-MnO}_2$ (321, 002, 332). The lattice constants shown in table 2 that AC has lattice constants close to $a = 2.456 \text{ \AA}$ and $c = 6.696 \text{ \AA}$ from graphite (JCPDS 41-1487). Meanwhile, MnO_2 has lattice constants close to $a = 9.920 \text{ \AA}$ and $c = 2.925 \text{ \AA}$ from $\alpha\text{-MnO}_2$ (JCPDS 44-0141). The use of $\alpha\text{-MnO}_2$ is due to larger pore size than other MnO_2 or other nano transition metal oxide, which supports the ions adsorption/desorption process [17]. The XRD pattern of the $\text{ACMnO}_2/\text{rGO}$ sample in Fig. 2b shows diffraction peaks at angles of 26.255° , 44.442° ,

64.854° , and 78.009° , corresponding to graphite (002, 101) and $\alpha\text{-MnO}_2$ (321, 002, 332). The lattice constants in table 3 show that AC and rGO also have lattice constants close to graphite, and MnO_2 has lattice constants close to $\alpha\text{-MnO}_2$.

Table 2. Lattice constants of ACMnO_2 sample.

2θ	JCPDS 2θ	hkl	Strain	d ($\text{\AA}$)	a ($\text{\AA}$)	c ($\text{\AA}$)
44.093	44.079	101	0.0003	2.053	2.487	6.785
	45.221	321	0.0249	2.053		
64.565	63.582	002	0.0155	1.443	9.919	2.885
77.745	76.836	332	0.0118	1.228		

Table 3. Lattice constants of $\text{ACMnO}_2/\text{rGO}$ sample.

2θ	JCPDS 2θ	hkl	Strain	d ($\text{\AA}$)	a ($\text{\AA}$)	c ($\text{\AA}$)
26.255	26.610	002	0.0133	3.390		
	44.079	101	0.0082	2.037	2.466	6.785
44.442	45.221	321	0.0172	2.037		
64.854	63.582	002	0.0200	1.437	9.920	2.874
78.009	76.836	332	0.0153	1.224		

The addition of rGO causes a diffraction peak at the 002 graphite plane to be the most dominant, which previously disappeared. Moreover, the intensity of diffraction peak at the angle of 44.442° corresponding to two compounds increase. The diffraction peaks of all compounds still appear and do not shift significantly, indicating that there is no reaction between all materials. Therefore, the properties of composite materials are a combination of the physical and chemical properties of each constituent material. Meanwhile, the crystallite size (D) is given by Scherrer's equation as follows:

$$D = \frac{K \lambda}{\beta \cos \theta} \quad (6)$$

in which K is the dimensionless shape factor, which has a typical value of about 0.9, and β is FWHM. The results in tables 4 and 5 show that the ACMnO_2 sample has an average crystallite size of $\bar{D} = 18.0 \pm 0.8 \text{ nm}$, and the $\text{ACMnO}_2/\text{rGO}$ sample has an average crystallite size of $\bar{D} = 18 \pm 3 \text{ nm}$.

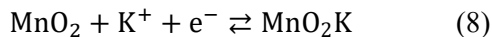
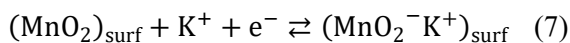
Table 4. Crystallite size of ACMnO_2 sample.

2θ	β	D (nm)
44.093	0.504	17.004
64.565	0.523	17.963
77.745	0.540	18.884

Table 5. Crystallite size of $\text{ACMnO}_2/\text{rGO}$ sample

2θ	β	D (nm)
26.255	0.570	14.307
44.442	0.501	17.140
64.854	0.488	19.287
78.009	0.484	21.116

AC and MnO_2 only have interfaces bonding and are uncompound [3]. Therefore, MnO_2 only has a reaction with ions from the electrolyte, which can be written as follows:



in which the oxidation states of Mn will change from +4 on MnO_2 to +3 on MnO_2K and $\text{MnO}_2^- \text{K}^+$. Eq. (7) shows the adsorption/desorption process of ions on the surface of MnO_2 , but with a smaller amount than the adsorption/desorption of ions on the carbon pores. Meanwhile, Eq. (8) shows the embedding/de-embedding process of cations near the surface or inside of MnO_2 , where the redox reaction takes place [18]. This process does not change the crystal structure of MnO_2 . Both equations show that cations have a significant role in the charge storage mechanism, which affects the performance of SCs.

The presence of fast and reversible redox reactions requires an electrolyte with high ionic conductivity and charge mobility. Therefore, using aqueous electrolytes is more appropriate than organic or ionic electrolytes. Although they suffer from a narrow operating potential window, the aqueous electrolytes can be easily managed in a laboratory without requiring a specific environment and are low-cost [19]. One of the favorite aqueous electrolytes, which is also used in this study, is KOH. Each ion has a bare ion size of 0.138 nm for K^+ and 0.110 nm for OH^- . Small ion size supports the large number of ions that can get into carbon pores. The K^+ ion has a conductivity of $73 \text{ cm}^2 \Omega^{-1} \text{ mol}^{-1}$ and mobility of $7.62 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1}$, which is higher than other cations such as Na^+ , Li^+ , and H^+ ions. Meanwhile, the OH^- ion has a conductivity of $198 \text{ cm}^2 \Omega^{-1} \text{ mol}^{-1}$ and mobility of $20.64 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1}$, which is higher than other anions such as Cl^- , NO_3^- , and SO_4^{2-} ions [20].

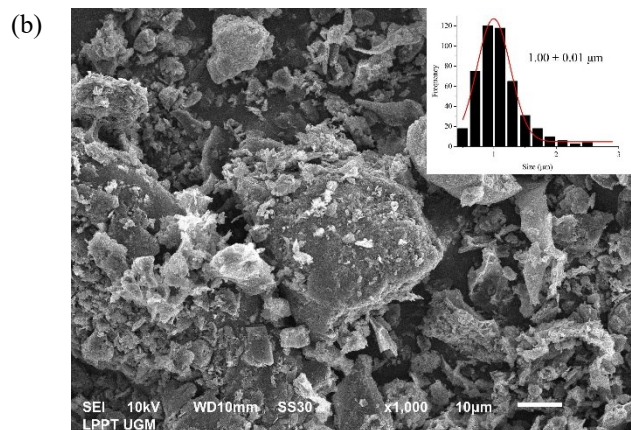
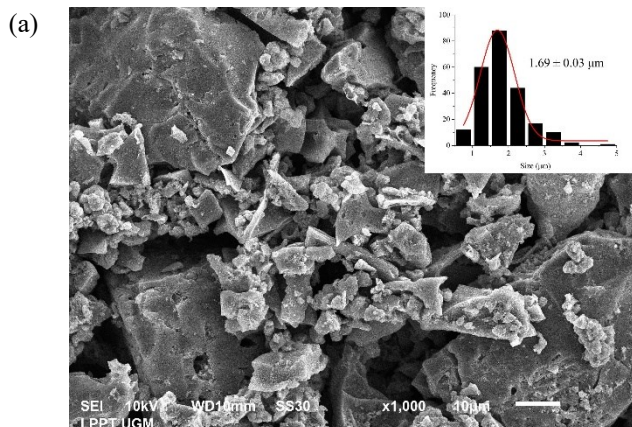
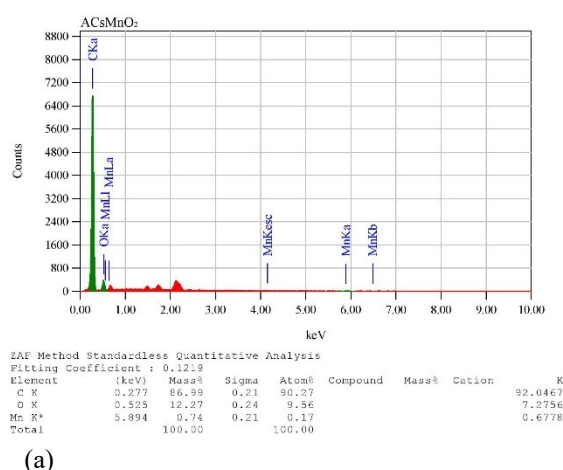
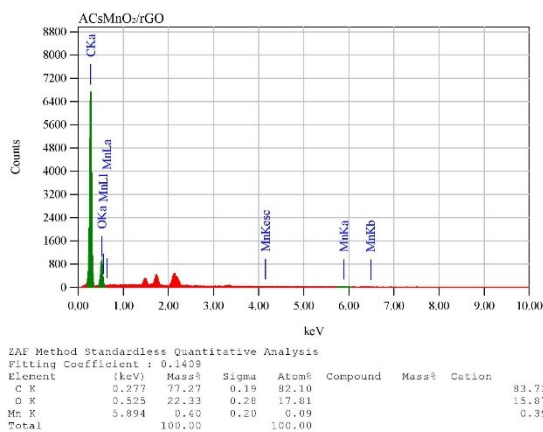


Fig. 3. Cross-sectional SEM image of (a) ACMnO_2 and (b) $\text{ACMnO}_2/\text{rGO}$ samples

Cross-sectional SEM images in Fig. 3 show that adding rGO through high heating temperature broke the surface of composite materials into smaller and more equal sizes, resulting in slight morphological changes. The smallest size average and distribution are obtained by using ImageJ and Origin software. The curve is shown as an inset in Figs. 3a and 3b, indicating a decrease of $0.69 \mu\text{m}$ and a loss of distribution above $3.00 \mu\text{m}$ after adding rGO. EDX test for the ACMnO_2 sample in Fig. 4a shows the mass percentage of the constituent elements, including carbon, oxygen, and manganese, which are 86.99%, 12.27%, and 0.74%, respectively. It also shows that the binder used is successfully eliminated in the synthesis process of ACMnO_2 , where PVDF material and DMF solution contain other elements such as hydrogen, fluorine, and nitrogen.





(b)
Fig. 4. EDX test of (a) ACMnO₂ and (b) ACMnO₂/rGO samples

EDX test in Fig. 4b also shows that the addition of rGO increased the mass and atomic percentage of the oxygen element by 82% and 86%, respectively but decreased the mass and atomic percentage of the carbon element by 11% and 9%, respectively. It indicates that the rGO used still has several stable oxygen functional groups which are not disappearing at the heating temperature of 350 °C. Meanwhile, the manganese element only has a small mass and atomic percentage, indicating the pseudocapacitance mechanism of MnO₂ has less contribution than the double-layer capacitance mechanism of carbon. Mapping tests also support the result of EDX tests. As shown in Fig. 5, the carbon element marked with red was dominant before the addition of rGO. However, after the rGO was added, the oxygen element marked with green was significantly increased on the surface morphology of the composite materials. Therefore, the method used in this research successfully ensured the rGO on top of the ACMnO₂ surface.

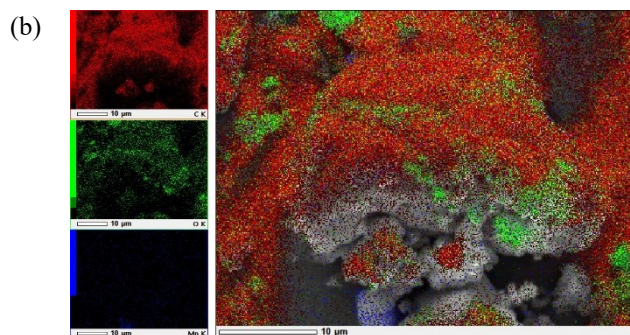
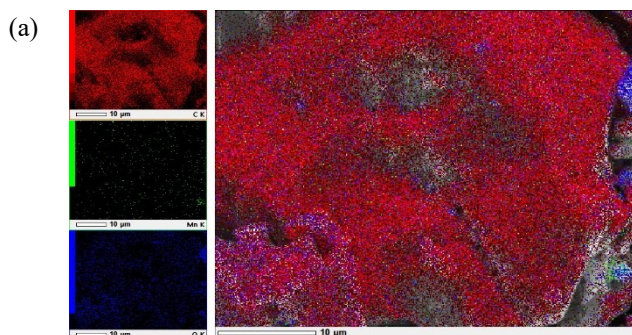


Fig. 5. Mapping test of (a) ACMnO₂ and (b) ACMnO₂/rGO samples

CONCLUSION

The addition of rGO on the surface of the ACMnO₂ composite material was achieved successfully by high heating temperature, where rGO decreased the smallest size average and distribution and increased the mass and atomic percentage of the oxygen element but did not cause the reaction with either AC or MnO₂. The SCs of the ACMnO₂/rGO composite electrode at a temperature variation of 350 °C obtained the highest specific capacitance of 459.79 F g⁻¹ at a scan rate of 9 mV s⁻¹, where the addition of rGO increased the specific capacitance by about 58% compared to without rGO.

For further research, it is still necessary to add other characterization methods such as Differential Scanning Calorimetry (DSC), Brunauer-Emmett-Teller (BET), and Transmission Electron Microscope (TEM) for the ACMnO₂/rGO composite electrode as well as Galvanostatic Cycling (GC) and Electrochemical Impedance Spectroscopy (EIS) for the SCs. Furthermore, variations can also be made on the SCs components such as a binder, separator, and electrolyte to make the SCs with different characteristics in both performance and flexibility.

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AUTHOR CONTRIBUTION

All authors contributed to the study's conception and design. Material preparation, data collection, and result analysis were performed by Adinandra Caesar Fachrudin. All authors read and approved the final version of the paper.

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