Effect of Composition Ratios on the Performance of Graphene/Carbon Nanotube/Manganese Oxide Composites toward Supercapacitor Applications

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ABSTRACT: Herein, we describe the preparation and characterization of graphene/carbon nanotube (CNT)/MnOₓ composites and the effects of chemical composition and phase transformation on the properties of the corresponding electrode film. In general, the effect of graphene-to-CNT ratio (G/C ratio) and the manganese (Mn) content on the morphology, chemical state, crystallization properties, and microstructure of the composite material was examined by scanning electron microscopy, X-ray photoelectron spectroscopy, X-ray diffraction, and selected area electron diffraction. The bonding mechanism between MnOₓ and graphite-based materials, that is, graphene and CNTs, is discussed. The influence of the composition of the composites on the performance of the electrode was investigated using charge-discharge curves. The faradically active MnOₓ also functioned as a considerable cobinder and allowed for a reduced amount of polymeric binder, which enhanced the conductivity and capacitance of the electrode. The optimized electrode composition was obtained based on our present graphene and CNT specifications. In summary, the results discussed in this article provide significant background information for future applications of graphene/CNT/MnOₓ composite electrodes.

1. INTRODUCTION

With the rapidly increasing demand for energy technologies in recent years, electroactive materials for various kinds of energy conversion and storage devices such as fuel cells, batteries, solar/thermoelectric/piezoelectric generators, and supercapacitors are being widely studied. 1–8 Among them, supercapacitors have attracted unique research attention because of their intrinsic features such as, high power density and excellent durability. 7,9,10

Considering the charge–discharge mechanism, supercapacitors can be classified into three major categories: electrochemical double-layer capacitors (EDLCs), pseudocapacitors, and hybrid capacitors. 9,11–13 In general, carbon-based materials such as activated carbon, carbon nanotubes (CNTs), graphene, mesoporous carbon, and carbon-fiber-based materials are frequently employed as the electrode material in EDLCs. 6,9,11,14–19 Each of these has its specific advantages and disadvantages. Among them, multiwall CNTs and single-layered graphene have attracted most research attention because of the corresponding long-term conductivity and high specific surface area (SSA), respectively. 18,19 However, in practice, the contact resistance is huge between CNT–CNT, CNT–graphene, and graphene–graphene owing to the large interface between the polymer binder and the nanoparticles. Moreover, CNT and graphene-based electrodes also suffer from winding into a group and piling up in stacks, respectively. 10,11,20,21 Integrating them together mitigates those problem to a certain extent. 7,10,11,20,22,23

Furthermore, when transition-metal oxides or electrically active polymers are involved in the electrodes, faradic redox reactions take place at the interface between them and the surrounding electrolytes during the charge–discharge process; these types of electrodes are known as pseudocapacitors. 9–11,22,24,25 Thus, EDLCs and pseudocapacitors are widely known for their higher power density and higher energy density compared to each other, respectively. Modification with these faradically active materials also helps to avoid the stacking of graphene. 36–28 Among various pseudocapacitive materials, manganese oxides (hereafter denoted as MnOₓ), including MnO, MnO₂, Mn₂O₃, Mn₃O₄, and Mn₂O₃ are promising candidates for active electrode materials for pseudocapacitors 9–11,22,23,25,26,29–36 due to their notable electrochemical capacity, wide potential range, low cost, and environmental friendliness.

For hybrid electrodes, graphene and CNT composites have been widely studied as EDLC materials. Recently many efforts have been made to blend manganese oxide with graphene and/or CNTs to obtain composites such as CNT/MnOₓ, graphene/MnOₓ, and graphene/CNT/MnOₓ and the results show that they exhibit higher specific capacitance and better cycle life compared to pure MnOₓ. 10,30–32,34 Generally, graphene and CNTs are expected to be ideal supporting
In contrast, when integrated with Mn (Spec. amorphous MnO$_2$ and G based materials and explains its behavior. Moreover, this article con
graphene/CNT/MnO$_2$. This suggests that other than COO$^-$ from the viewpoint of metallurgy, manganese also has a chemical affinity to carbon, and thus it is known to form phases of manganese carbides such as, MnC, Mn$_3$C, Mn$_5$C$_2$, Mn$_7$C$_3$, and Mn$_{13}$C$_6$. However, from the viewpoint of metallurgy, manganese also has a chemical affinity to carbon, and thus it is known to form phases of manganese carbides such as MnC, Mn$_3$C, Mn$_5$C$_2$, Mn$_7$C$_3$, and Mn$_{13}$C$_6$. This suggests that other than COO$^-$–Mn linkage, there are other possibilities for linkages between the metal oxide and graphite-based materials ($G_{based}$).

Therefore, to optimize the properties of EDLCs, tremendous attempts have been made to match, mix, and integrate multiple carbon materials together through a variety of methods. Moreover, various oxides or hydroxides of metals or bimetals, such as Ru, Co, Ni, Fe, Ce, Ni, Mn, V, Bi, Mo, and Ti, have been investigated to make various possible permutations and combinations. Recently Saeed et al, reported a novel 3-dimensional graphene/CNTs/MoO$_3$ hybrid film as an advance electrode material for asymmetric supercapacitors. In addition, the manufacturing technology of supercapacitors has matured. Furthermore, the capacitance and performance also depend on the packaging technology and equipment; therefore, it is more valuable to work systematically toward a specific purpose rather than to compete for the highest capacitance. For instance, methods have been specifically devised to increase the conductivity, energy density, cost performance, decrease the binder content, and to better understand the mechanism of electron or ion transfer.

In this study, MnO$_2$ was used as the faradic active material as well as a binder, allowing for the exclusion of the insulating polymer binder. The effects of graphene-to-CNT ratio (G/C ratio) on the morphology, Mn content on crystallization, and polyvinylidene fluoride (PVDF) content on resistance were analyzed to study the effect of all these on the capacitive behavior. Moreover, this article confirms the binding between amorphous MnO$_2$ and $G_{based}$ materials and explains its potential for significantly reducing polymer binder content. The optimized condition was determined based on the adopted graphene and CNT specifications. Finally, the results presented here provide valuable building blocks for the future development of composite electrodes for supercapacitors.

2. RESULTS AND DISCUSSION

2.1. Integration and Characterization of Materials.

2.1.1. MnO$_2$ as a Binder and the Effect of Graphene-to-CNTs Ratio (G/C Ratio) on the Morphology of the Composite.

The dispersion and morphology of graphene and CNT mixtures were analyzed via scanning electron microscopy (SEM) observations. Figure 1a shows the SEM images of a graphene and CNT mixture (Spec.: $G_6C_2$). It is clear that CNTs tend to entangle each other, and that there are four groups of tangled CNTs, as marked with dotted circles in Figure 1a. The corresponding magnified images are shown in Figure 1a(i–iv). In contrast, when integrated with Mn (Spec.: $G_6C_2$–M$_{25}$), the graphene/CNT/MnO$_2$ composites dispersed well without piling up or entangling each other (Figures 1b and S1c–f). These results strongly suggest that MnO$_2$ is not only a faradically active material, but it could also significantly act as a cobinder, providing better adhesion between graphene and CNTs.

Furthermore, considering the effect of the G/C ratio on the morphology of the composite, SEM images of graphene/CNT/MnO$_2$ composites with a constant Mn content (25 wt %) were obtained. Figure S1c–f shows that, upon using 25 wt % MnO$_2$ as the binder, graphene (Figure S1a) and CNTs (Figure S1b) mixed well and were dispersed easily at the G/C ratios of 9/1, 8/2, 7/3, and 5/5. Even at a G/C ratio of 2/8 (Figure S1g), it is obvious that each graphene sheet is isolated in the CNT framework. This result illustrates that graphene and CNTs are dispersed well at all G/C ratios when using MnO$_2$ as a binder, which is potentially useful for a wide range of electrode applications. In brief, the optimized graphene/CNT mixing condition with minimum stacking of graphene can be obtained with the method reported herein.

2.1.2. Effect of Mn Content on the Morphology of the Composite.

As the capacitance of the material may be influenced by the variation in morphology caused by varying the Mn content, specimens with 10, 15, 20, 25, 30, 35, and 40 wt % of Mn (i.e., Spec.: $G_6C_2$–M$_{10}$, $G_6C_2$–M$_{15}$, $G_6C_2$–M$_{20}$, $G_6C_2$–M$_{25}$, $G_6C_2$–M$_{30}$, $G_6C_2$–M$_{35}$, and $G_6C_2$–M$_{40}$ respectively)
were analyzed by SEM and transmission electron microscopy (TEM) (Figure S2a–g). The obtained SEM and TEM images agree with the conclusions drawn in the previous section, that is, graphene and CNT can be well dispersed by adding MnO. The Mn content of these composites was examined by SEM-energy-dispersive X-ray spectrometry (EDS) analysis, indicating 10.3, 15.9, 21.1, 24.4, 35.6, and 40.6 wt % of Mn in G8C2-M10, G8C2-M15, G8C2-M20, G8C2-M25, G8C2-M30, G8C2-M35, and G8C2-M40, respectively. The SEM and TEM images of G8C2 and G8C2-M10 in Figures 1a and S2(a–1), respectively, indicate that in a composite with 10 wt % Mn, MnO was well dispersed and can be observed only by TEM (Figure S2(a–1)) and not by SEM (Figure S2a). The MnO particles with the average dimension of 10 × 40 nm are randomly dispersed on graphene and CNTs. Upon increasing their content to 15 wt %, the MnO particles start to agglomerate to form particles with a size of up to ca. 250 nm (as observed in Figure S2b). As the Mn content increased to 20, 25, 30, 35, and 40 wt %, the size of the MnO particle grew up to ca. 350, 600, 900, 1500, and 2000 nm, respectively. Because higher specific capacitance should be obtained with better dispersion,40 optimized specific capacitance (F/g) was expected to be obtained with 10 wt % of MnO. However, phase transformation was also observed with particle agglomeration, which results in a positive effect on specific capacitance, which will be discussed in Section 2.2.2.

2.1.3. Microstructure of the Composite. The microstructure of the specimens was investigated by TEM analyses to probe the contact between graphene/CNTs and MnO. The TEM images of functionalized CNTs (Spec.: G6C10) and CNT/MnOx (Spec.#: G6C10-M15) in Figure 2a,b, respectively, suggest that the functionalized CNTs can be fully covered with a MnO layer with a thickness of approximately 15–20 nm. Figure 2c,d shows the corresponding high-resolution TEM and selected area electron diffraction (SAED) images of specimen CNT/MnOx indicating that the whole MnO phase is in an amorphous state. In contrast, the TEM images of graphene and graphene/MnOx (Spec.#: G10C0 and G10C0-M15) in Figure 3a,b, respectively, indicate that MnOx is randomly attached to the graphene sheets. Figure 3c shows the corresponding high-resolution TEM image, in which most of the MnO phase is in an amorphous state with a few nanocrystals embedded in the amorphous phase. The diffraction spots reside along the rings in the SAED image (Figure 3d), thus proving the existence of both amorphous and nanocrystalline MnOx on the graphene surface. These observations prove that our proposed MnOx blending process helps MnOx to bond well with the Gbased materials, as well as provide hints that MnOx could also act as a binder for Gbased electrode materials, as reported.41 Considering graphene/CNT/MnOx ternary composites, for instance, Figure S2(a–1) evidently supports our speculation; it shows that MnOx randomly binds graphene and CNTs together.

X-ray photoelectron spectroscopy (XPS) analyses were conducted to understand the mechanism of how amorphous MnOx binds with both the CNTs and graphene. Figure 4 shows the XPS C 1s spectrum of CNTs, graphene, and their respective composites with MnOx (Spec.: G6C10, G6C10-M15, G10C0, G10C0-M15). As reported earlier by Rosillo-Lopez and Salzmann, the binding energy of COOH (at ca. 289 eV) shifts to 288 eV, suggesting the formation of COO–Mn.9,10,22,37 Considering the variation from CNT to CNT/MnOx observed in the deconvoluted spectra (Figure 5), the −COOH peak at ca. 288.85 (Spec.# G10C10) shifted to ca. 288.35 which corresponds to −COOMn (Spec.# G10C10-M25). This is in agreement with the previous reports that state that −COOMn bonding assists MnOx bonding to CNT.5,10,22,37 However, this explanation only partially supports our assumption regarding Mn bonds with the Gbased materials. Consider that in single-layered graphene, only a trace amount of −COOH groups and −COOMn bonding can be identified in the XPS C 1s spectra of G10C0 and G10C0-M15, respectively.
Furthermore, the amorphous MnO\textsubscript{v} is randomly dispersed on the graphene surface (as seen in Figures 2 and S2(a-1)). In other words, there may be another type of bonding that exists between the MnO\textsubscript{v} and G-based materials. After integrating with MnO\textsubscript{v}, the XPS C 1s spectra shown in Figure 5 shows an obvious peak shift, from C–OH bonding at 285.70 eV (CNT and graphene) to 285.35 eV, which is attributed to the formation of the C–OMn bond. These results suggest the possibility of C–OMn sharing a larger portion of the bonding between MnO\textsubscript{v} and G-based materials than C–OH.

Figure 6 shows the deconvoluted XPS O 1s spectra of functionalized CNTs, MnO\textsubscript{v}, and their composite (Spec. #: G\textsubscript{0}C\textsubscript{10}, MnO\textsubscript{v}, G\textsubscript{0}C\textsubscript{10}–MnO\textsubscript{v}, G\textsubscript{10}C\textsubscript{0}, and G\textsubscript{10}C\textsubscript{0}–MnO\textsubscript{v}). As can be seen, on one hand, the presence of oxygen on CNT can be attributed to the presence of –COOH, where the peaks at 531.2, 533.1, and 532.3 eV correspond to C=O, –COOH, and C=OH, respectively. On the other hand, the peaks at 529.4, 530.8, and 532.05 eV represent Mn–O, Mn–OH, and H–O–H in MnO\textsubscript{v}, respectively. The peak corresponding to the binding energy at 529.4 eV represents Mn–O, whereas the peak at 531.3 eV denotes C–O–Mn, Mn–OH, and C=O (Figure 6). These are the possible major bonding modes in the CNT/MnO\textsubscript{v} composite. Furthermore, it is impossible to deconvolute the peak at 531.3 eV into separate C–O–Mn, Mn–OH, and C=O peaks, which makes it clear that the –COOH and C–OH peaks have almost disappeared in the O 1s region of the XPS spectrum of CNT/MnO\textsubscript{v} (as indicated by the dotted line in Figure 6). Instead, the C–O–Mn bond plays a major role in the binding of CNT and MnO\textsubscript{v}, where C–O–Mn may represent the formation of bonding through both CNT–OMn and CNT–COOMn. This result agrees with the results drawn from the XPS analysis of the C 1s region. According to the above discussion, a scheme is proposed to illustrate how MnO\textsubscript{v} binds to G-based materials (shown in Figure S4). First, –COOH groups are formed accompanied with a greater number of –OH groups (Figure S4a). Consider that the red bond [in Figure S4 (a-left)] illustrates the bond that be reacted during the acid treatment, and Figure S4(a-right) illustrates that after the acid treatment (the removal of red bonds), the carbon atom may connect the G-based materials through one C–C bond (blue bond) or three C–C bonds (green bonds); in other words, it could be the C (red atoms) in –COOH group or could be the C (orange atoms) connecting to –OH group. This model suggests that the acid strength, reaction temperature, reaction time, and graphitization degree may affect the –OH/–COOH ratio. Figure S4b also demonstrates how the MnO\textsubscript{v} can bind well with functionalized G\textsubscript{based} materials through the O–Mn and COO–Mn bonds.

As discussed earlier, Mn also has a chemical affinity to carbon and MnC, Mn\textsubscript{2}C, Mn\textsubscript{3}C\textsubscript{2}, Mn\textsubscript{4}C\textsubscript{9}, and Mn\textsubscript{13}C\textsubscript{6} are the possible manganese carbides. However, there is a lack of literature reports discussing this mechanism. In the XPS analyses, it was known that the M–C (M = metal) binding

Figure 5. Deconvoluted XPS spectra of C 1s region for CNTs, graphene, and their composite with 25 wt % MnO\textsubscript{v} (Spec. #: G\textsubscript{0}C\textsubscript{10}, G\textsubscript{0}C\textsubscript{10}–MnO\textsubscript{v}, G\textsubscript{10}C\textsubscript{0}, and G\textsubscript{10}C\textsubscript{0}–MnO\textsubscript{v}).

Figure 6. XPS O 1s spectra of CNTs, MnO\textsubscript{v}, and their composite (Spec. #: G\textsubscript{0}C\textsubscript{10}, MnO\textsubscript{v}, G\textsubscript{0}C\textsubscript{10}–MnO\textsubscript{v}, G\textsubscript{10}C\textsubscript{0}–MnO\textsubscript{v}).

C=O peaks, which makes it clear that the –COOH and C–OH peaks have almost disappeared in the O 1s region of the XPS spectrum of CNT/MnO\textsubscript{v} (as indicated by the dotted line in Figure 6). Instead, the C–O–Mn bond plays a major role in the binding of CNT and MnO\textsubscript{v}, where C–O–Mn may represent the formation of bonding through both CNT–OMn and CNT–COOMn. This result agrees with the results drawn from the XPS analysis of the C 1s region.
energy in the metal carbide should be slightly lower than that of a sp²-hybridized carbon (C–C–sp³) in the C 1s region and lower than that of MnO in the Mn 2p region.\textsuperscript{44,45} However, there is no noticeable manganese carbide peaks to be identified in the C 1s or Mn 2p regions (in Figures 4 and S5), implying that there is not a considerable amount of manganese carbide in our composite. In brief, both CNT–OMn and CNT–COOMn are the only bonding possibilities, and CNT–COMn and CNT–Mn bonds are not possible between C\textsubscript{0} based materials and MnO\textsubscript{x} in the synthesized composite materials.

With regard to the chemical state of Mn in the composite, the XPS Mn 2p spectrum of pure MnO\textsubscript{x} has examined and deconvoluted, as shown in Figure 7. The results suggest that the XPS Mn 2p3/2 spectrum of pristine MnO\textsubscript{x} reveals that there is approximately 77.4% Mn\textsubscript{3}O\textsubscript{4} and Mn\textsubscript{2+}, Mn\textsubscript{3+}, and Mn\textsubscript{4+}, respectively. Other than pure MnO\textsubscript{x}, the XPS Mn 2p spectra of CNT/MnO\textsubscript{x} graphene/MnO\textsubscript{x} and graphene/CNT/MnO\textsubscript{x} (i.e., Spec.\# G\textsubscript{0C10-M25-P10}, G\textsubscript{10C0-M25-P10}, G\textsubscript{5C5-M25-P10}, G\textsubscript{2C8-M25-P10}, G\textsubscript{8C2-M25-P10}, G\textsubscript{7C3-M25-P10}, G\textsubscript{10C0-M25}) show no differences and thus have the same chemical states, as shown in Figure S5. Here, Mn\textsuperscript{4+} represents the existence of MnO\textsubscript{2}, and the Mn\textsuperscript{3+}/Mn\textsuperscript{2+} ratio is consistent with the ratio of 2/1 in Mn3O4.\textsuperscript{44,45} Thus, the XPS spectra revealed that there is approximately 77.4% MnO\textsubscript{2} and 22.6% MnO\textsubscript{x} in MnO\textsubscript{x} in our materials, where subscript \( v \) equals to 1.4.

2.2. Factors Affecting the Capacitance. 2.2.1. Effect of Graphene-to-CNT (G/C) Ratio. To determine the effect of the G/C ratio on the capacitance, electrodes made with different G/C ratios, that is, Spec.\# G\textsubscript{10C0-M25-P10}, G\textsubscript{9C1-M25-P10}, G\textsubscript{8C2-M25-P10}, G\textsubscript{7C3-M25-P10}, G\textsubscript{6C4-M25-P10}, G\textsubscript{5C5-M25-P10}, G\textsubscript{4C6-M25-P10}, G\textsubscript{3C7-M25-P10}, G\textsubscript{2C8-M25-P10}, G\textsubscript{1C9-M25-P10}, G\textsubscript{0C10-M25-P10}, and G\textsubscript{2C8-M25-P10} were examined with chronopotentiometric (CP) measurements under a current density of 1 A/g, as depicted in Table 1. The trends are clearly illustrated in Figure 8a, and the parameters are collected in Table 1. These results indicate that when the G/C ratios are 10/0 and 0/10, the capacitances obtained are 102 and 83 F/g, respectively; this is due to the SSA of the adopted single-layered graphene (436.7 m\textsuperscript{2}/g) being significantly greater than that of the multiwalled CNTs (31.9 m\textsuperscript{2}/g). However, the graphene layers tend to pile up in stacks, which blocks most of the active surface, and hence it is impossible for G\textsubscript{10C0} to perform to its potential capacity.\textsuperscript{10,11,20,21} It also is clear that, with the addition of MnO\textsubscript{x}, the specific capacity of G\textsubscript{10C0-M25-P10} increased obviously. This improvement could be attributed to both the faradic capacitances of MnO\textsubscript{x} and the decreased stacking of graphene layers.

As shown in Figure 8, the capacitance of G\textsubscript{vCw-MzP} is enhanced with an increase in the CNT content, and reaches the maximum value of 146 F/g, at a G/C ratio of 8/2. Further increase in the CNT content leads to a linear decrease in the capacitance, which suggested that minimized graphene stacking can be reached at a G/C ratio equal to or smaller than 8/2. However, the capacitance decline with a further increase in the CNT content, for Spec.\# G\textsubscript{vCw-MzP} and Spec.\# G\textsubscript{vCw-MzP} can be attributed to the lower specific capacitance (SSA) of CNTs. In brief, because graphene tends to pile up in stacks during the electrode drying process, adding lower content of CNTs helps to avoid this detrimental stacking. The optimized G/C ratio that delivers a higher capacitance value was found to be 8/2.

2.2.2. Effect of Mn-to-Carbon Ratio. To examine the effects of the Mn content on the capacitance of the materials, CP measurements were conducted with specimens G\textsubscript{vCw-MzP} (where \( y = 0, 10, 15, 20, 25, 30, 35, \) and 40), based on the G/C ratio of 8/2 discussed in the previous section. As shown in Figure 9, the results indicate that all CP curves are pseudo-triangular. Without MnO\textsubscript{w}, G\textsubscript{vCw-MzP} has a capacitance of only 30 F/g. With the addition of MnO\textsubscript{x} even the MnO\textsubscript{2} phase started to agglomerate into particles ranging from several tens of nm to 900 nm in size, the capacitance increased from 68 to 181 F/g as the Mn content increased from 10 to 30 wt %. It is worth noting that the specimen with only 25 wt % Mn (i.e., G\textsubscript{vCw-MzP} capacitance: 146 F/g) displayed higher capacitance than pure MnO\textsubscript{x} (i.e., MnO\textsubscript{2}, capacitance: 128 F/g), as depicted in Table 1. Upon increasing the Mn content further from 30 to 40 wt %, the size of the agglomerated MnO\textsubscript{x} grew quickly to 2000 nm and caused declining capacitance.

Phase transformation of MnO\textsubscript{x} as the particle agglomeration takes place, could have some effect on the specific capacitance. As summarized in the previous section, MnO\textsubscript{x} on one hand

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**Figure 7.** XPS Mn 2p spectrum of pristine MnO\textsubscript{x}.

**Figure 8.** (a) Galvanostatic charge–discharge curves of G\textsubscript{vCw-MzP}; \( v \) and \( w \) represent the amount of graphene and CNTs and \( w/x \) ranges from 0/1 to 1/0; (b) variation of the capacitance as a function of the CNT content.
consists of \( \sim 77.4\% \) Mn\(_3\)O\(_4\) and 22.6\% MnO\(_2\). On the other hand, according to the observed X-ray diffraction (XRD) patterns of graphene/CNT/MnO\(_v\) composites (shown in Figure 10; Spec. #: G\(_8\)C\(_2\)-M\(_{35}\)y-P10, where \( y \) ranges from 10 to 35), while adding 10–25 wt % of Mn, it is hard to identify any crystalline peaks of Mn\(_3\)O\(_4\) and MnO\(_2\). Subsequently, increasing the Mn content to 30 wt %, the obvious characteristic peaks correspond to Mn\(_3\)O\(_4\) appeared, which matched the standard data card of Mn\(_3\)O\(_4\) (JCPDS 08-0017). The existence of Mn\(_3\)O\(_4\) is consistent with our prediction from the XPS analyses. Besides the crystalline phase has higher conductivity, and it has been reported that normal spinel-structured Mn\(_3\)O\(_4\) with Mn\(^{2+}\) in tetrahedral units and Mn\(^{3+}\) in octahedral units exhibits higher capacity than MnO\(_2\).33,35

Table 1. Specimen Designation and Properties

| Specimen designation | G/C ratio | Mn (wt %) | MnO\(_v\) particle size (nm) | Specimen designation | PVDF (wt %) | Super-P (wt %) | Capacitance (F/g) | Sheet resistance, \( R_s \) |
|----------------------|-----------|-----------|-----------------------------|----------------------|-------------|-----------------|-------------------|---------------------|
| p-CNT 0/10 0 N/A     | p-CNT-P10 | 10 10 5  N/A |
| p-G\(^{a}\) 10/0 0 N/A | p-G-P10 10 10 102 N/A |
| f-C\(^{a}\) 0/10 0 N/A | f-C-P10 10 10 83 N/A |
| MnO\(_v\) N/A 71\(^{b}\) | MnO\(_v\)-P10 10 10 128 N/A |
| G\(_8\)C\(_2\)-M\(_{35}\) 10/0 25 G\(_8\)C\(_2\)-M\(_{35}\)-P10 10 10 102 |
| G\(_8\)C\(_2\)-M\(_{35}\) 9/1 25 G\(_8\)C\(_2\)-M\(_{35}\)-P10 10 10 122 |
| G\(_8\)C\(_2\)-M\(_{35}\) 8/2 25 G\(_8\)C\(_2\)-M\(_{35}\)-P10 10 10 146 |
| G\(_8\)C\(_2\)-M\(_{35}\) 7/3 25 G\(_8\)C\(_2\)-M\(_{35}\)-P10 10 10 131 |
| G\(_8\)C\(_2\)-M\(_{35}\) 5/5 25 G\(_8\)C\(_2\)-M\(_{35}\)-P10 10 10 113 |
| G\(_8\)C\(_2\)-M\(_{35}\) 2/8 25 G\(_8\)C\(_2\)-M\(_{35}\)-P10 10 10 95 |
| G\(_8\)C\(_2\)-M\(_{35}\) 0/10 25 G\(_8\)C\(_2\)-M\(_{35}\)-P10 10 10 83 |
| G\(_8\)C\(_2\)-M\(_{35}\) 8/2 0 N/A G\(_8\)C\(_2\)-M\(_{35}\)-P10 10 10 10 N/A |
| G\(_8\)C\(_2\)-M\(_{35}\) 8/2 10 10 \times 40 nm\(^{2}\) G\(_8\)C\(_2\)-M\(_{35}\)-P10 10 10 68 |
| G\(_8\)C\(_2\)-M\(_{35}\) 8/2 15 250 nm G\(_8\)C\(_2\)-M\(_{35}\)-P10 10 10 85 |
| G\(_8\)C\(_2\)-M\(_{35}\) 8/2 20 350 nm G\(_8\)C\(_2\)-M\(_{35}\)-P10 10 10 103 |
| G\(_8\)C\(_2\)-M\(_{35}\) 8/2 25 600 nm G\(_8\)C\(_2\)-M\(_{35}\)-P10 10 10 146 |
| G\(_8\)C\(_2\)-M\(_{35}\) 8/2 30 900 nm G\(_8\)C\(_2\)-M\(_{35}\)-P10 10 10 181 0.06355 |
| G\(_8\)C\(_2\)-M\(_{35}\) 8/2 35 1500 nm G\(_8\)C\(_2\)-M\(_{35}\)-P10 10 10 156 |
| G\(_8\)C\(_2\)-M\(_{35}\) 8/2 40 2000 nm G\(_8\)C\(_2\)-M\(_{35}\)-P10 10 10 128 |
| G\(_8\)C\(_2\)-M\(_{35}\) 8/2 30 G\(_8\)C\(_2\)-M\(_{35}\)-P1 3 10 101 0.04897 |
| G\(_8\)C\(_2\)-M\(_{35}\) 8/2 30 G\(_8\)C\(_2\)-M\(_{35}\)-P1 5 10 210 0.05447 |
| G\(_8\)C\(_2\)-M\(_{35}\) 8/2 30 G\(_8\)C\(_2\)-M\(_{35}\)-P1 7 10 194 0.06044 |
| G\(_8\)C\(_2\)-M\(_{35}\) 8/2 30 G\(_8\)C\(_2\)-M\(_{35}\)-P1 10 10 181 0.06355 |
| G\(_8\)C\(_2\)-M\(_{35}\) 8/2 30 G\(_8\)C\(_2\)-M\(_{35}\)-P3 15 10 161 0.07113 |

\(^{\text{a}}\)Specific surface areas of graphene, CNT, and G\(_8\)C\(_2\)-M\(_{35}\) composite are 463.7, 31.9, and 158.3 m\(^2\)/g, respectively.

\(^{\text{b}}\)71 wt % Mn in MnO\(_v\) was calculated considering the subscript \( v \) equals to 1.4, according to the XPS results discussed in Section 2.1.3.

Figure 9. (a) Galvanostatic charge−discharge curves of G\(_8\)C\(_2\)-M\(_{35}\)y-P10 and (b) variation of the capacitance as a function of Mn content in G\(_8\)C\(_2\)-M\(_{35}\)y-P10 composite, where \( y \) represents the Mn content in the electrode film, which ranges from 0 to 40 wt %.

Figure 10. XRD patterns of G\(_8\)C\(_2\)-M\(_{35}\) composite materials, where \( y \) ranges from 10 to 35.

35), while adding 10–25 wt % of Mn, it is hard to identify any crystalline peaks of Mn\(_3\)O\(_4\) and MnO\(_2\). Subsequently, increasing the Mn content to 30 wt %, the obvious characteristic peaks correspond to Mn\(_3\)O\(_4\) appeared, which matched the standard data card of Mn\(_3\)O\(_4\) (JCPDS 08-0017). The existence of Mn\(_3\)O\(_4\) is consistent with our prediction from the XPS analyses. Besides the crystalline phase has higher conductivity, and it has been reported that normal spinel-structured Mn\(_3\)O\(_4\) with Mn\(^{2+}\) in tetrahedral units and Mn\(^{3+}\) in octahedral units exhibits higher capacity than MnO\(_2\).33,35
However, no such characteristic peaks corresponding to MnO₂ was seen in any of the XRD patterns, which suggests that 22.6 wt % of MnO₂ tends to be in the amorphous state, whereas aggregation takes place during our experimental conditions. Therefore, the amorphous MnO₂ phase is considered to bind to graphene and CNTs (Figure S4). In brief, the phase transformation from amorphous to spinel Mn₃O₄ confers higher capacitance, whereas the MnO₂ phase remains in the amorphous phase and binds with the G₈C₂-M based materials.

Other than phase transformation, the particles agglomerated to an average diameter of 900 nm (in Figure S2e) were also examined by EDS mapping (shown in Figure S6). The EDS map shows that the particle consists of 43, 37, and 20 at. % of carbon, oxygen, and manganese, respectively, suggesting that the agglomerated particles are actually a mixture of carbon (43 wt %) and MnO₂. In other words, the nanostructure of the carbon/MnO₂ mixture may also contribute to a certain extent to the capacitance and reduce the effect of agglomeration on the total specific capacitance.

In summary, as the Mn content increases to 30 wt %, the capacitance found increased to 181 F/g and is accompanied by the crystallization of Mn₃O₄ and the agglomeration of the carbon/MnO₂ mixture. On extending this limit, serious agglomeration of particles is the primary cause of declining capacitance.

2.2.3. Effect of the PVDF Content on the Capacitance. In addition to the effect of each active component, such as manganese, graphene, and CNTs, the effect of binder (PVDF) content on our proposed materials was also examined by the CP and electrochemical impedance spectra (EIS) analyses. The charge–discharge curves and capacitance variation trends are shown in Figure 11a. Figure 11b shows the capacitance variation trends with increasing PVDF content. Upon decreasing the PVDF content from 15 to 5 wt %, the capacitance increases linearly from 161 to 210 F/g, which is reasonable because less isolated PVDF would block less of the active area, and the material would have better conductivity. As shown in Figure 11a, IR drop can be clearly observed upon adding 15, 10, and 7 wt % PVDF (Spec. #: G₈C₂-M₃₀-P₁₅, G₈C₂-M₃₀-P₁₀, and G₈C₂-M₃₀-P₇). Upon decreasing the PVDF content to 5 wt %, the IR drop is greatly mitigated (Spec. #: G₈C₂-M₅₀-P₃). These results suggest that the conductivity can be significantly improved by reducing the PVDF content to 5 wt %.

Figure 12 shows the EIS spectrum of the electrodes with different binder (PVDF) contents ranging from 15 to 3 wt %.

Figure 11. (a) Galvanostatic charge–discharge curves of G₈C₂-M₃₀-P₇, and (b) variation of the capacitance with the PVDF content in G₈C₂-M₃₀-P₇ composite, where z represents the PVDF content in the electrode film, which ranges from 3 to 15 wt %.
3. CONCLUSIONS

We have successfully demonstrated that MnO₂ particles can bind and disperse well with CNTs and graphene to form graphene/CNT/MnO₂ ternary composite electrodes. With the addition of MnO₂ as a binder, the graphene and CNTs were dispersed well, which helped avoid the piling up and the entanglement of graphene and CNTs. The optimized G/C ratio is found to be 8/2. The proposed graphene/CNTs/MnO₂ composite materials can be obtained with the addition of 30 wt % of Mn. According to the results obtained from XPS analyses, a scheme was proposed to explain how MnO₂ binds with functionalized G-based materials. The −COOH functionalization is accompanied by a greater amount of −OH groups, which would be converted to COO−Mn and O−Mn bonds that connect the G-based materials and MnO₂. Moreover, the manganous oxide (MnO₂) used in this study is found to be composed of 77.4% crystallized Mn₃O₄ and 22.6% amorphous MnO₂. MnO₂ has proved to serve as both a faradic material and a cobinder, which improved the capacitance and reduced the content of the PVDF binder. Finally, the optimized electrode material (i.e., GₓCᵧ−M₃O₄) showed a high capacitance of 210 F/g with only 5 wt % PVDF, performed a high cycle stability of 91.0% after 1000 cycles, and achieved a maximum power density of 8619 W/Kg and energy density of 51.5 W h/kg.

4. EXPERIMENTAL SECTION

4.1. Pretreatment of CNTs. CNTs purchased from Hodogaya Chemical (NT-7, diameter of 65 nm, SSA = 139 m²/g) were pretreated with an acid solution containing 4.5 M nitric acid and 1.5 M sulfuric acid. Typically, 0.5 g of CNTs were dispersed and stirred in 100 mL of acid solution at 45 °C for 3 h. The functionalized CNTs were then filtered and collected using a Büchner funnel and washed with deionized (DI) water and dried. The functionalized CNT powder was then used for preparing the composite electrode.

4.2. Synthesis of Graphene/CNT/MnO₂ Composites. Graphene/CNT, graphene/MnO₂, CNT/MnO₂ and graphene/CNT/MnO₂ composite materials were prepared by dispersing the desired amounts of graphene, CNT, and MnO₂ in acetone. Graphene powder [N002-PDR, Angstrom Materials Inc. (AMI)] with less than 3-graphene layers, x−y dimensions of up to 10 × 10 μm², and average SSA of 400−800 m²/g was used in this study. The solution was placed in a sealed glass bottle and sonicated for 30 min to obtain a uniform dispersion. Subsequently, 10 mL of ethylene glycol was added as a reducing agent, and the resulting mixture was sonicated for another 30 min. The mixture was then loaded into a Teflon-lined autoclave and heated at 150 °C for 2 h. The resulting composite material was washed with DI water and dried overnight at 60 °C.

4.3. Preparation of Electrodes. Carbon black Super-P, PVDF, and N-methyl-2-pyrrolidione (NMP) at a desired ratio were added together and stirred for 3 h at 100 °C. Super-P served as the conducting agent and PVDF as the binder. Each of the dried composite powder specimens listed in Table 1 was then added to the Super-P/PVDF/NMP solution. Uniform slurries were then obtained after stirring for 1 h. The slurries were subsequently scraped onto 316L stainless steel sheets (20 mm × 40 mm × 0.1 mm) through a fixed template (10 mm × 20 mm × 0.1 mm). The obtained electrodes were then dried at 100 °C in a circulating oven.

4.4. Specimen Designation. A series of composites were designed for the active materials and investigated to understand the effects of graphene-to-CNT ratio (G/C ratio) and the Mn and PVDF contents on the properties of the composite electrode. As shown in Table 1, the materials such as pure CNT, functionalized CNT, pure graphene, and manganese oxides are denoted as p-CNT, f-C, p-G, and MnOₓ, respectively. Graphene and CNT mixtures are referred to as GₓCᵧ; the corresponding specimens integrated with MnO₂ are referred to as GₓCᵧ−M₃. The corresponding electrodes bound with the PVDF binder are denoted as GₓCᵧ−M₃−Pₓ. The suffixes “w” and “x” represent the G and C content in weight ratio; the suffix “v” represents the Mn content in the graphene/CNT/MnO₂ composite material, and the suffix “z” stands for the PVDF content (wt %) of the electrodes.

4.5. Characterization. All composite electrode specimens listed in Table 1 were analyzed ex situ and in situ. For ex situ experiments, SEM (JSM-7100F) was used to observe the surface morphology, TEM (JEOL JEM-2100, 200 keV) was used to examine the microstructure, and XRD analysis (PANalytical X’Pert PRO, Cu Kz radiation, λ = 0.1541 nm) was used to verify the crystal structure and phase. Nitrogen adsorption/desorption analysis was carried out under 77 K (Micromeritics, ASAP2020) and used to determine the SSA. EDS was employed to determine the electrode compositions and the XPS (ULVAC-PHI PHI 5000 VersaProbe) was used to determine the composition and chemical state of specimens shown in Table 1.

For in situ analyses, a CP technique was employed to determine the capacitance (C) of each specimen. Typically, the CPs were recorded with the response voltage (V) and time (s) under the desired charge−discharge current (mA) in the range of −0.2 to 0.8 V. As each electrode had a different weight, the current was normalized by mass (unit of A/g) for ease of comparing the results between different electrodes. In this study, half-cell test analyses were done to conclude the optimized electrode composition. The CP measurements were carried out in a three-electrode cell using 1 M Na₂SO₄ solution as the electrolyte, with Pt and Ag/AgCl as the counter and reference electrodes, respectively. Instead of using glassy carbon or graphite rods, a stainless-steel sheet, which provides a high electrode area (200 mm²) and thus excellent accuracy, was utilized as the support for the working electrode. The EIS were then measured with signals operating at a frequency range between 30 mHz and 1000 kHz.

The gravimetric capacitances were calculated according to eq 1, where I is the charge−discharge current, Δt stands for the time differential, m represents the mass of the active electrode material, and ΔV is the voltage range of scanning segments. The cell device capacitance Cₑ, energy density (Dₑ), and power density (Dₚ) were calculated from the cyclic chronopotentiometric curves, according to eqs 2 and 3.

\[
C_i = \frac{I \times \Delta t}{m \times \Delta V} \tag{1}
\]

\[
D_e = \frac{1}{2} C_e (\Delta V^2) \tag{2}
\]

\[
D_p = \frac{D_e}{\Delta t} \tag{3}
\]
SEM, TEM, and EDS mapping images of specimens; O 1s and Mn 2p regions of XPS spectra of specimens; scheme to explain how MnO\(_2\) bind to CNT and graphene; variation of specific capacitance with cycle number; and Ragone plot of the proposed composite (PDF)

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Notes

The authors declare no competing financial interest.

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