Effect of Potassium Ions on the Formation of Mixed-Valence Manganese Oxide/Graphene Nanocomposites

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Abstract: One-pot synthesis of mixed-valence manganese oxide (MnO\textsubscript{x})/potassium ion-doped reduced graphene oxide (rGO) composites for efficient electrochemical supercapacitors is introduced. Using manganese nitrate and potassium permanganate as co-precursors for the MnO\textsubscript{x} and by directly annealing the rGO without tedious purification steps, as described herein, MnO\textsubscript{x}/rGO composites with a high specific capacitance of 1955.6 F g\textsuperscript{-1} at a current density of 1 A g\textsuperscript{-1} are achieved. It is found that the presence of potassium ions helps in the development of mixed-valence MnO\textsubscript{x} on the surface of the rGO.

Keywords: manganese oxide; reduced graphene oxide; nanocomposite; graphene

1. Introduction

Recently, composite electrode materials comprising electrochemical double-layer capacitors (EDLCs) and pseudocapacitors have come to represent a promising avenue for providing greater energy density for supercapacitors. The use of a pseudocapacitive material enables fast electron transfer at the surface of the electrode, leading to a higher energy density than can be achieved by using EDLCs alone. As a promising candidate for a composite electrode material, nanocomposites composed of manganese oxide (MnO\textsubscript{x}) and graphene have been widely investigated [1–8]. The properties of graphene, such as high electrical conductivity, large specific surface area, transparency, and flexibility, are beneficial to use as a supercapacitor electrode material [9–17]. Manganese oxide is attractive as a pseudocapacitor because of its low cost, natural abundance, environmental compatibility, and high theoretical specific capacitance [18]. The shortcoming of manganese oxide as a pseudocapacitor electrode is its lack of electrical conductivity, which can be compensated for by the use of graphene composites. In addition, the high surface area and high electrical conductivity of graphene can improve the electrochemical performance by double layer formation, and this is also helped by a uniform distribution of the manganese oxides on the basal plane of the graphene.

The electrochemical performance of the manganese oxides are directly influenced by their crystal structures and oxidation states. Several studies have reported on how the electrochemical performance depends on the oxidation states of manganese oxides [19,20]. In particular, it is reported that the presence of mixed-valence manganese oxides can result in superior performance of capacitive behavior, due to the coexistence of aliovalent manganese cations that drive the defect-accelerated kinetics of the surface reactions [21].
In this study, we report on a one-pot synthesis of a mixed-valence manganese oxide (MnO<sub>x</sub>) potassium (K<sup>+</sup>) ion-doped, reduced graphene oxide (rGO) composite materials for an efficient supercapacitor electrode. By using manganese nitrates and potassium permanganate as co-precursors for MnO<sub>x</sub> and then using direct annealing without any intervening washing steps, mixed-valence MnO<sub>x</sub>/rGO composites with a K<sup>+</sup>-doped rGO structure were successfully achieved. Due to the synergetic effects created by the presence of mixed-valence MnO<sub>x</sub> and K<sup>+</sup> ions, the resulting composite structure showed excellent capacitive properties, reaching a maximum specific capacitance of 1955.6 F g<sup>-1</sup> at a current density of 1 A g<sup>-1</sup>.

2. Materials and Methods

2.1. Materials

H<sub>2</sub>SO<sub>4</sub> (98%), H<sub>2</sub>O<sub>2</sub> (35%), and HCl (5%) were purchased from Dae-Jung (Suwon, Korea). Graphite flakes, KMnO<sub>4</sub>, manganese (II) nitrate tetrahydrate (Mn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O), KOH, activated carbon, N-methyl-2-pyrrolidone (NMP), and polyvinylidene fluoride (PVDF) were purchased from Sigma-Aldrich (Steinheim, Germany). All of these materials were used without any further purification.

2.2. Preparation of GO

A modified Hummers’ method was used to prepare the Graphite oxide (GO), as described in previous reports [22]. Briefly, 2 g of graphite flakes were mixed with 46 mL of 98% sulfuric acid in a 250 mL round bottom flask and placed in an ice bath with constant stirring. Then 6 g of potassium permanganate was slowly added to the mixture. After 2 h, the supernatant mixture was transferred to an oil bath and kept at a constant temperature of 35 °C for 6 h. Then 92 mL of de-ionized (DI) water was gradually added to the reaction mixture. The mixture was then stirred for 1 h. The whole reaction mixture was then poured into a 1 L beaker containing 240 mL of water. Then 35% hydrogen peroxide solution was added until the color of the mixture changed to bright yellow. Hydrochloric acid diluted in 5% water was added in order to remove the metal cations. Finally, the resulting solution was washed with DI water, and dialysis was performed until a neutral graphite oxide solution was obtained.

2.3. Preparation of MnO<sub>x</sub>/rGO Nanocomposites

100 mg of GO was uniformly dispersed in 200 mL of DI water using water bath sonication for 1 h. Then 20 mL each of 0.01 M Mn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O and KMnO<sub>4</sub> solutions were simultaneously added, dropwise, to the GO solution with stirring at a constant speed for 1 h. The supernatant mixture was then dried at room temperature, and finally the remaining moisture was removed by vacuum drying at room temperature. No washing with water was involved in this process. The resulting solid powder-type mixtures were annealed at 500 °C in an Ar atmosphere. For a comparative study, samples annealed at 400 °C and 600 °C were also prepared and compared for their electrochemical performances.

2.4. Characterization

A Tecnai G2 F20 (FEI, Hillsboro, OR, USA) was used to take transmission electron microscopy (TEM) images and perform energy dispersive X-ray spectroscopy (EDS) analysis. X-ray diffraction (XRD) patterns were recorded on a Rigaku SmartLab diffractometer (Rigaku, Tokyo, Japan) using Cu Kα radiation. A Jobin Yvon LabRAM HR UV-Visible-NIR spectrometer (Horiba, Kyoto, Japan) was used to obtain Raman spectra. X-ray photoelectron spectroscopy (XPS) information was obtained on a Thermo Fisher Scientific (Waltham, MA, USA) K-alpha using an Al source. Fourier transform infrared (FT-IR) spectra were recorded on a JASCO (Tokyo, Japan). A Verios 460L (FEI, Hillsboro, OR, USA) was used to take field emission scanning electron microscope (FE-SEM) images and also used to perform energy dispersive spectroscopy (EDS) mapping analysis.
2.5. Electrochemical Measurements

Electrochemical responses of the MnOx/rGO composites were measured using a three-electrode system. A 6 M KOH aqueous solution was used as the electrolyte, a platinum plate was used as the counter electrode, and Ag/AgCl was used as the reference electrode. The working electrode was prepared by mixing 80 wt% active material, 15 wt% activated carbon, and 5 wt% polyvinylidene fluoride (PVDF) in N-methyl-2-pyrrolidone (NMP). The slurry was then spread onto a glassy carbon electrode, which was used as the current collector. The electrode was then heated at 60 °C for 24 h to evaporate the solvent. The rate of total deposited mass throughout our study was 1.5 mg cm⁻². To investigate the electrochemical performance of the electrodes, cyclic voltammetry (CV) and galvanostatic charge-discharge techniques were employed. Electrochemical performance in the three-electrode configuration was determined in a CH660D electrochemical station (CH Instruments, Inc., Austin, TX, USA).

3. Results and Discussion

3.1. Materials Characterization

The MnOx/rGO nanocomposites were synthesized using manganese nitrate and potassium permanganate as co-precursors for the MnOx. First, electrostatic binding of manganese (II) cations on the surface of GO was achieved. With the addition of potassium permanganate, permanganate (MnO₄⁻) ions were bonded with Mn²⁺ ions. Subsequent annealing at 500 °C in an Ar atmosphere led to the resulting MnOₓ/K⁺-doped rGO composites. No washing was involved in this process; therefore, abundant K⁺ ions were introduced in the composite structure. The X-ray diffraction (XRD) patterns of the compositions and crystal structures of the MnOₓ/rGO nanocomposites and the GO are shown in Figure 1a. Sharp characteristic peaks corresponding to the MnOₓ on the surface of the graphene appeared at 23.1°, 30.0°, 31.7°, 34.9°, 40.5°, 47.3°, 58.7°, 70.1°, and 73.7°, indicating the presence of mixed-valence MnOₓ including MnO, Mn₂O₃, and Mn₃O₄, which was confirmed by Joint committee on powder diffraction standards (JCPDS) No. 07-0230 (MnO), JCPDS No. 00-041-1442 (Mn₂O₃), and JCPDS-International Center for diffraction data (ICDD) No. 00-07-0230 (Mn₃O₄), respectively. It was found that using the annealing temperature of 500 °C was beneficial for the development of the mixed-valence manganese oxides in this work (Figure 1b). At lower annealing temperatures, such as 300 °C or 400 °C, negligible peaks of manganese oxides were detected, indicating that such annealing temperatures were insufficient for the development of MnOₓ crystals. In addition, when the annealing temperature reached 600 °C, most MnOₓ were thermally converted to a Mn₂O₃ single phase [23]. The nominal peaks of K⁺-intercalated MnOₓ structure (KₙMn₈O₁₆) was also detected alongside in case of the composite annealed at 500 °C.

![Figure 1](image-url)
Typical microstructures of the MnOx/rGO nanocomposites, investigated by TEM, are shown in Figure 2. As seen in Figure 2a, MnOx nanoparticles in the range of 6 to 12 nm grew on the surface of the graphene sheets. Our proposed approach allowed us to achieve uniformly distributed MnOx particles without nanoparticle aggregation. The loaded amount of the MnOx on the surface of the graphene can be controlled by varying the amounts of precursors used for the growth of the MnOx. Figure 2b shows a lattice spacing of 2.6 nm, which corresponds to the (111) plane of MnO. Figure 2c shows the 0.28 nm lattice spacing of the (200) plane of Mn3O4. Figure 2d shows the 0.26 nm lattice spacing of the (222) plane of the Mn2O3. The MnOx phase is found to be one of the following: MnO, Mn2O3, and Mn3O4. In addition, the nominal presence of the K+-intercalated MnOx structures were observed through TEM analyses (Figure S1), which are in agreement with the XRD results.

![Figure 2](image_url)

**Figure 2.** (a) A typical transmission electron microscopy (TEM) image of GM500, and the enlarged TEM images which reveal the structures of (b) MnO, (c) Mn3O4, and (d) Mn2O3.

Figure 3 displays the TEM-EDS maps showing the distributions of C, O, Mn, K, and K-Mn in combination. It also shows that the K+ ions were uniformly distributed on the rGO surface and near the grain boundary of the polymorphs of the MnOx. Also, a small amount of the K+ ions were detected within the MnOx structure (Figure 3e,f). This is due to the small number of K+-intercalated MnOx structures present in the composites, which is in accordance with the XRD study. During calcination at 500 °C, it is known that NO3 ions can easily evaporate, but K+ ions remain stably along the grain boundary of the polymorphs of MnOx, as well as on the surface of the rGO [24].

The Raman spectra of the GO and the MnOx/rGO nanocomposite are shown in Figure 4a. A D band at 1346 cm⁻¹ and a G band at 1570 cm⁻¹ were detected in the spectrum of GO. The characteristic D and G bands are observed for both the MnOx/rGO nanocomposite and the GO products. The intensity ratios of the D to G bands for GO and the MnOx/rGO nanocomposite show an obvious change: 0.75 and 0.98, respectively. The increasing value of the D/G intensity ratio of the MnOx/rGO nanocomposite...
in comparison to that of the GO is due to the reduced size of the sp² domains and the creation of new graphitic domains with smaller sizes after thermal reduction at 500 °C [25]. In addition, the peaks at 639.7 cm⁻¹ for the MnOₓ/rGO are assigned to the Mn–O stretching vibration in the basal plane of MnO₆ and/or the symmetric stretching vibration of the MnO₆ group [26].

Figure 3. Energy dispersive spectroscopy (EDS) analysis of GM₅₀₀ with TEM. (a) TEM image of GM₅₀₀, elemental maps of (b) C, (c) O, (d) Mn, and (e) K, and the (f) Mn-K composite image.

Figure 4. (a) Raman spectra of the GO and GM₅₀₀. (b) X-ray photoelectron spectroscopy (XPS) survey scan of GM₅₀₀. (c) Mn 2p region, and (d) Mn 3s region of GM₅₀₀.
The surface electronic state and the chemical bonding state of MnO\textsubscript{x}/rGO were analyzed in detail by XPS. As shown in Figure 4b, the survey XPS spectrum for the MnO\textsubscript{x}/rGO nanocomposite revealed the presence of carbon, manganese, potassium, and oxygen. In particular, the omission of the rinsing step after the reaction of the KMnO\textsubscript{4} in the preparation of the MnO\textsubscript{x}/rGO nanocomposite may account for the presence of the K\textsuperscript{+} inside the MnO\textsubscript{x}/rGO after annealing. The C 1s peak originates from the graphene nanosheets. The Mn 2p peak was further inspected by high-resolution XPS analysis, as shown in Figure 4c. The two peaks at 641.5 eV and 653.2 eV can be assigned to Mn 2p\textsubscript{3/2} and 2p\textsubscript{1/2}, respectively, which are characteristic of mixed-valence MnO\textsubscript{x} \cite{27,28}. The oxidation state of the manganese was confirmed by the multiplet splitting of the Mn 3s state. As shown in Figure 4d, the splitting width was 5.5 eV, which is in accordance with a previous report on the XPS spectrum of Mn\textsubscript{3}O\textsubscript{4} \cite{19}. Fourier transform infrared spectroscopy (FT-IR) was used to characterize the GO and the MnO\textsubscript{x}/rGO nanocomposites, and the results are shown in Figure S2. The GO showed a broad band at 3300–3700 cm\textsuperscript{-1} and a distinct band at 1620~1730 cm\textsuperscript{-1}, corresponding to O–H and C=O, C–O respectively. After the composite was made, all bands decreased significantly, and a new peak, for the MnO\textsubscript{x} band, at 600 cm\textsuperscript{-1} was confirmed \cite{29–31}.

3.2. Electrochemical Properties

To evaluate the temperature-dependent electrochemical behavior and quantify the capacitance performance of the MnO\textsubscript{x}/rGO nanocomposites, samples annealed at 400 °C, 500 °C, and 600 °C were prepared, and cyclic voltammetry (CV) measurements were taken at different scan rates under the operating potential of −0.6–0.7 V in a three-electrode system. The results are shown in Figure 5a. It can be observed that GM\textsubscript{500} shows a larger capacitive area than either GM\textsubscript{400} or GM\textsubscript{600}. This is because the pseudocapacitance is dependent on the structure of the metal oxide. Recently, it was established that a multivalent oxide system is capable of adsorbing anions as well as transporting the oxygens into vacant sites of manganese ions, thus promoting high redox reactions and faster electron transitions \cite{32,33}. From the above XRD study, we observed that the crystal structure and the valence state of the resulting MnO\textsubscript{x} and the following CV performances are dependent on the annealing temperature. GM\textsubscript{400} showed very low capacitive current compared to GM\textsubscript{500}, probably due to the insufficient growth of the mixed-valence MnO\textsubscript{x}. GM\textsubscript{600} also demonstrated an inferior performance to that of GM\textsubscript{500}. This is attributed to the reduced redox active formation of the Mn\textsubscript{3}O\textsubscript{4}, which could, in turn, result in a reduction of the capacitive current for the increased annealing temperature of 600 °C. However, upon annealing at 500 °C, various mixed-valence MnO\textsubscript{x} phases, such as MnO, Mn\textsubscript{2}O\textsubscript{3}, and Mn\textsubscript{3}O\textsubscript{4}, were generated, which is found to be beneficial for a larger capacitive current area.

A CV analysis of GM\textsubscript{500} at different scan rates was carried out to investigate the current response of GM\textsubscript{500}. All of the CV curves had a quasi-rectangular shape for both low and high scan rates (Figure 5b). Typically, at the high scan rates—above 50 mV s\textsuperscript{-1}—the CV curves are distorted from their rectangular shape. This indicates unbalanced ion diffusion with respect to the charging and discharging currents, caused by the polarization between the metal oxide and electrolyte with limited incubation of electrolyte inside the electrode materials. However, the graphs are almost the same with respect to the zero-current axis. To quantify the capacitance value of GM\textsubscript{500}, we conducted galvanostatic charge/discharge measurements. Figure 5c shows a faint hump in the 0.09 V signal during charging, and a slight bend appears in the discharging graph. This is due to the significance of the redox reaction during electrochemical performance, which varies due to the presence of the mixed-valence MnO\textsubscript{x} and the abundant K\textsuperscript{+} ions. Figure 5d presents specific capacitance values calculated from the following equation:

$$C_s = \frac{2i_m \int V \, dt}{V_f^2} \bigg|_{V_i} \, (1)$$
where $C_s$ (F g$^{-1}$) is the specific capacitance, $i_m = I/m$ (A g$^{-1}$) is the current density, where $I$ is the current and $m$ is the mass of the active material, $\int Vdt$ is the integral current area, where $V$ is the potential with initial and final values of $V_i$ and $V_f$, respectively [34].

![Figure 5](image-url)

**Figure 5.** Cyclic voltammetry (CV) curves for (a) GM400, GM500, and GM600 at a scan rate of 10 mVs$^{-1}$, (b) CV curves of GM500 at various scan rates, (c) Galvanostatic charge-discharge curves of GM500 at different current densities, and (d) Specific capacitance vs. current density plot for GM500.

The highest and lowest specific capacitance values were 1955.6 F g$^{-1}$ and 840.7 F g$^{-1}$ at current densities of 1 A g$^{-1}$ and 4.5 A g$^{-1}$, respectively. These high capacitive performances might be due to the presence of the K$^+$ ions on the grain boundary of the MnO$_x$ and the surface of the rGO, which were easily transported from the electrode to the electrolyte. In previous studies, the charge storage mechanisms of MnO$_x$-based composites were controlled mainly by the intercalation/de-intercalation of alkali cations and the structural changes that occurred during the electrochemical performances [35]. In our study, most of the K$^+$ ions were doped on the surface of the rGO, rather than intercalated within the MnO$_x$. Since the K$^+$ ions doped on the rGO induce an n-doping effect of graphene, the electrical conductivity of the rGO is expected to be enhanced [18]. In this regard, transportation of electrons from the redox center to the current collector can be promoted, resulting in an increase of capacitance performance. Moreover, the formation of mixed-valence MnO$_x$ can result in superior performance of capacitive behavior, which benefits from the coexistence of aliovalent manganese cations that drive the defect-accelerated kinetics of the surface reactions. Both GM400 and GM600 show capacitive properties inferior to that of GM500, which indicates that during the annealing process, there is insufficient development of the mixed-valence MnO$_x$ (Figures S3 and S4). In addition, GM500 exhibited the largest surface area, 210 m$^2$ g$^{-1}$, from Brunauer-Emmet-Teller (BET) analysis (Belsorp-max, Bel Japan Inc., Toyonaka, Japan) compared to that of GM400 and GM600, supporting the superior capacitive property of GM500 (Figure S5). The cyclic stability test results shown in Figure 6 reveal that the specific capacitance is retained as 96%, even after 4000 charge/discharge cycles. Based on these results, we conclude that GM500 is an effective material for use as a supercapacitor electrode.
To clarify the effect of the K$^+$ ions, GM$_{500}$ without K$^+$ ions was also prepared. K$^+$-free GM$_{500}$ was prepared by repetitive washing after the reaction of the manganese precursors and subsequent annealing at 500 °C. From TEM and XRD studies, it is found that the resulting K$^+$-free GM$_{500}$ is composed of Mn$_3$O$_4$, without showing any multivalency (Figure S6). We employed scanning electron microscopy (SEM) and EDS mapping to compare the composition of elements before and after washing the GM$_{500}$ (Figure 7). The EDS elemental mapping image of GM$_{500}$ showed the K-edge signals of Mn, O, and K with atomic percentages of 22%, 39%, and 39%, respectively (Figure 7a). In contrast, the EDS mapping of K$^+$-free GM$_{500}$ indicates an increased amount of O and a dramatically decreased amount of K after washing. The atomic percentages of Mn, O, and K were 9%, 84%, and 7%, respectively (Figure 7c). Figure 7b shows the XPS survey scan of the K$^+$-free GM$_{500}$, presenting an absence of bonding associated with K ions. The above results indicate that the K$^+$ ions are removed by washing. The electrochemical performances also show that K$^+$-free GM$_{500}$ is very inferior to GM$_{500}$ with K$^+$ doping, exhibiting a specific capacitance of 272 F/g at a current density of 1 A/g (Figure 7d). From these observations, we can conclude that the presence of K$^+$ ions is essential for developing multi-valence MnO$_x$ on the surface of the rGO upon annealing at a temperature of 500 °C, leading to the superior capacitive performance of the composite electrode.

![Figure 6. Cyclic stability of GM$_{400}$, GM$_{500}$, and GM$_{600}$ at a current density of 1.0 A g$^{-1}$.](image_url)

![Figure 7. (a) Scanning electron microscopy (SEM) and EDS of GM$_{500}$. (b) XPS survey scan of K$^+$-free GM$_{500}$. (c) SEM and EDS of K$^+$-free GM$_{500}$. (d) Specific capacitance versus current density of K$^+$-free GM$_{500}$.](image_url)
4. Conclusions

In conclusion, we presented a facile synthesis of mixed-valence MnO$_x$/K$^+$-doped rGO nanocomposites for efficient supercapacitor electrodes. By using the electrostatic binding of the manganese precursor and KMnO$_4$, and subsequent annealing, we successfully fabricated the MnO$_x$/rGO composites with uniformly distributed MnO$_x$ on the surface of K$^+$-doped rGO. The abundant K$^+$ ions remaining on the surface of the rGO helps to develop mixed-valence MnO$_x$ and leads to a superior capacitive property by promoting a faster reversible reaction. Furthermore, it was found that an annealing temperature of 500 °C was suitable for sufficient growth of mixed-valence MnO$_x$/rGO nanocomposites. The resulting composite materials yield a specific capacitance of 1955.6 F g$^{-1}$ at 1 A g$^{-1}$, which demonstrates that these K$^+$-doped MnO$_x$/rGO nanocomposites would be attractive for various energy applications.

Supplementary Materials: The following are available online at http://www.mdpi.com/1996-1944/12/8/1245/s1, Figure S1: TEM image showing nominal presence of K$^+$-intercalated MnO$_x$ on the surface of the rGos. The lattice spacing corresponds to (200) plane of K$_6$Mn$_3$O$_{16}$. Figure S2: FT-IR spectra of the GO and the MnO$_x$/rGO composites. Figure S3: (a) GCD curves of GM$_{400}$; (b) specific capacitance variation of GM$_{400}$ according to the change of current density; (c) GCD curves of GM$_{600}$; (d) specific capacitance variation of GM$_{600}$ according to the change of current density. Figure S4. Electrochemical impedance spectroscopy (EIS) plots of GM$_{400}$, GM$_{500}$, and GM$_{600}$. Figure S5. BET surface area analysis of the GM$_{500}$. Figure S6. K$^+$-free GM$_{500}$ prepared from repetitive washing. (a) SEM; (b) TEM; (c) XRD data shows that the washed GM$_{500}$ is composed of Mn$_3$O$_4$ single phase.

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Conflicts of Interest: The authors declare no conflict of interest.

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