Synthesis and Electrochemical Characterization of Reduced Graphene Oxide-Manganese Oxide Nanocomposites

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ABSTRACT:
Nanocomposites of reduced graphene oxide and manganese (II,III) oxide can be synthesized by the freeze-drying process of the mixed colloidal suspension of graphene oxide and manganese oxide, and the subsequent heat-treatment. The calcined reduced graphene oxide-manganese (II,III) oxide nanocomposites are X-ray amorphous, suggesting the formation of homogeneous and disordered mixture without any phase separation. The reduction of graphene oxide to reduced graphene oxide upon the heat-treatment is evidenced by Fourier-transformed infrared spectroscopy. Field emission-scanning electronic microscopy and energy dispersive spectrometry clearly demonstrate the formation of porous structure by the house-of-cards type stacking of reduced graphene oxide nanosheets and the homogeneous distribution of manganese ions in the nanocomposites. According to Mn K-edge X-ray absorption spectroscopy, manganese ions in the calcined nanocomposites are stabilized in octahedral symmetry with mixed Mn oxidation state of Mn(II)/Mn(III). The present reduced graphene oxide-manganese oxide nanocomposites show characteristic pseudocapacitance behavior superior to the pristine manganese oxide, suggesting their applicability as electrode material for supercapacitors.

Keywords: Reduced graphene oxide, nanocomposite, manganese oxide, pseudocapacitance, porous structure

Introduction
Recently supercapacitors attract intense research interest as auxiliary power source for hybrid electric vehicles and plug-in electric vehicles. The electrochemical activity of many transition metal oxides is investigated to develop new efficient electrode materials with high energy density, high power density, and excellent rate characteristics. Among various transition metal oxides, low price, rich abundance, low toxicity, and diverse oxidation states of manganese element render its oxides promising electrode materials for supercapacitors and lithium secondary batteries. Since the formation of electron double layer and the redox reactions of electrode component near the surface are responsible for the charge storage capability of supercapacitors, it is important to increase the surface area of manganese oxide through the formation of nanostructures. Thus, various types of nanostructured manganese oxides such as 0D nanoparticles/hollow spheres, 1D nanowires/nanorods/nanotubes, 3D nanounch, and mesoporous materials are synthesized and many of them are applied as electrode for supercapacitors. To further improve the electrode performance of nanostructured manganese oxides, it would be useful to couple these nano-materials with conductive carbon species. The resulting enhancement of electrical conductivity can make better the electrode performance of manganese oxide. As a new family of nanostructured...
carbon, 2D graphene nanosheets receive particular attention because of their high electrical conductivity and high morphological anisotropy. Since the exfoliated graphene nanosheets are lack of lattice energy stabilization along the c-axis, they can easily hybrid with foreign species. As homologues to graphene nanosheets, the subnanometer-thick nanosheets of layered manganese oxide can be synthesized by soft-chemical exfoliation of the layered K$_{0.45}$MnO$_2$. This layered MnO$_2$ nanosheet can be transformed into different type of manganese oxide nanocrystals upon the heat-treatment. Thus, the nanocomposite of reduced graphene oxide and manganese oxide would be synthesized by the sedimentation of the mixed colloidal suspension of graphene oxide and exfoliated manganate nanosheets and the following heat-treatment at elevated temperature.

In the present study, homogeneous nanocomposites of reduced graphene oxide-manganese (II,III) oxide are synthesized by the freeze-drying process of the mixed colloidal suspension of graphene oxide and manganese oxide, and the following calcination process. The crystal structure, crystal morphology, and chemical bonding nature of the obtained materials are examined with diffraction, microscopic, and spectroscopic tools. Their electrode activity is investigated to probe the electrode functionality of the obtained manganese oxide-based materials.

**Experimental**

**Preparation**

Layered potassium manganese oxide K$_{0.45}$MnO$_2$ and its protonated derivative were prepared by the solid state reaction with the stoichiometric mixture of K$_2$CO$_3$ and MnO$_{2}$ at 800°C, and the reaction of the obtained K$_{0.45}$MnO$_2$ powder with 1 M HCl aqueous solution at room temperature for 4 days. The exfoliated nanosheets of layered manganese oxide were obtained in the form of stable aqueous colloidal suspension by the intercalation of tetrahexylammonium (TBA) cations into the protonated manganese oxide. The exfoliated nano-sheets of reduced graphene oxide were prepared by modified Hummer method: the homogeneous suspension of graphite oxide (150 ml) was reacted with 150 ml of distilled water, 150 ml of hydrazine solution (35 wt% in water), and 1.05 ml of aqueous ammonia solution (28 wt% in water). The vigorous stirring of the resulting suspension in a water bath (~85°C) for 1 h led to the formation of the colloidal suspension of reduced graphene oxide. Both the aqueous colloidal suspensions could be homogeneously mixed with each other. The mixing ratio of manganate:graphene oxide for the formation of the nanocomposites was adjusted as 2 : 1, 1 : 1, and 1 : 2 (The obtained nanocomposites were denoted as MGO2 : 1, MGO1 : 1, and MGO1 : 2, respectively). The powdery nanocomposites were restored from these mixed colloidal suspensions via freeze-drying process. For the reduction of graphene oxide in the nanocomposites, the as-prepared MGO nanocomposites (MGO2 : 1, MGO1 : 1, and MGO1 : 2) were heated at 300°C under N$_2$ flow for 3 h (The calcined nanocomposites were denoted as RMGO2 : 1, RMGO1 : 1, and RMGO1 : 2, respectively).

**Characterization**

Powder X-ray diffraction (XRD) analysis was carried out to study the crystal structure of graphene oxide-manganese oxide nanocomposites before and after the heat-treatment. Their crystal morphology and chemical composition were probed by field emission-scanning electron microscopy (FE-SEM) and energy dispersive spectrometry. The optical property of the nanocomposites was examined by measuring UV-vis absorption spectroscopy. The chemical bonding nature of the nanocomposites was investigated with Fourier transformed infrared (FT-IR) spectroscopy and Mn K-edge X-ray absorption spectroscopy (XAS). The present XAS spectra were measured with the extended X-ray absorption fine structure (EXAFS) facility installed at the beam line 7C at the Pohang Accelerator Laboratory (PAL) in Korea. XAS data were measured in a transmission mode using gas-ionization detectors. The energy of the Mn K-edge XAS data was referenced to the spectrum of Mn metal foil. The experimental spectra were analyzed by the standard procedure reported previously.

**Electrochemical Measurement**

The electrochemical activity of the reduced graphene oxide-manganese oxide nanocomposites was studied by measuring cyclic voltammograms (CV) and galvanostatic charge-discharge cycles of these materials. These electrochemical properties of the present materials were characterized with conventional three-electrode cell and a potentiostat/galvanostat (WonA Tech). The working electrode materials were prepared by mixing the nanocomposite, acetylene black, and polyvinylidenefluoride (PVDF) in a mass ratio of 75 : 20 : 5. After stirring the mixtures for 1 h in N-methylpyrrolidone, the resulting slurry was pressed on a stainless steel substrate. The stainless steel plate was used as substrate for composite
electrode material and as a current collector. The resulting composite electrode was vacuum-dried at 80°C for 30 min. A platinum mesh and saturated calomel electrode (SCE) were used as a counter electrode and a reference electrode, respectively. 0.2 M aqueous solutions of alkali metal sulfates (Li$_2$SO$_4$, Na$_2$SO$_4$, and K$_2$SO$_4$) were employed as electrolyte. CV data were collected in the potential range from 0 to 1.0 V at a scan rate of 20 mV s$^{-1}$. A constant current density of 200 mA g$^{-1}$ was applied for the galvanostatic charge-discharge cycling.

Results and Discussion

Powder XRD Analysis

The powder XRD patterns of the as-prepared graphene oxide-manganese oxide nanocomposites and their calcined derivatives are plotted in Fig. 1, compared with those of the reassembled nanosheets of graphene oxide and layered manganese oxides.

The reassembled nanosheets of exfoliated layered manganate restored from the corresponding colloidal suspension show well-developed (00l) reflections, reflecting the formation of TBA-intercalated layered manganate phase. Conversely, no distinct XRD peak can be observed for the reassembled graphene oxide nanosheets, suggesting that the monolayer of graphene oxide is too thin to form well-ordered intercalation structure. Instead, this material displays a very broad hump peak at 20 ~ 20-30°, indicating the disordered stacking of exfoliated graphene oxide nanosheets. After the hybridization with graphene oxide, a series of (00l) XRD peaks newly appear at lower angle compared with those of the reassembled layered manganese oxide, suggesting the lattice expansion of layered manganate along the c-axis. As the content of graphene oxide increases, the intensity of newly observed Bragg reflections becomes stronger. This finding suggests that the new XRD peaks originate from the interstratification structure of layered manganates monolayers and graphene oxide nanosheets with a high degree of hydration. The basal spacing calculated from the newly appeared XRD peaks is estimated as ~24.8-27.6 Å, which is much larger than that of the reassembled manganese oxide (~16.7 Å). After the heat-treatment at 300°C, all of the (00l) peaks in the nanocomposites are suppressed. Instead, a broad peak at 20 ~ 20-30° is still observable, suggesting the formation of the disordered assembly of exfoliated nanosheets. No observation of distinct XRD peaks strongly suggests that manganese oxide is homogeneously mixed with reduced graphene oxide nanosheets without any phase separation.

FE-SEM Analysis

The morphological change of the graphene oxide-manganese oxide nanocomposites before and after the heat-treatment is examined with FE-SEM analysis. The FE-SEM images of the as-prepared nanocomposites and their calcined derivatives are presented in Fig. 2. Wave-like surface morphology formed by the stacking of exfoliated nanosheets is detected for all the present reassembled nanocomposites. After the heat-treatment at 300°C, all the nanocomposites show house-of-cards type porous stacking structures of reduced graphene oxide sheets. Plenty of pores appear in the stacked structure of all the calcined nanocomposites. The other nanocomposite materials composed of restacked layered MnO$_2$ nanosheets show similar morphology in the FE-SEM images.

The N$_2$ adsorption-desorption isotherm measurement for these nanocomposite materials clearly demonstrated the formation of porous structure with expanded surface area. Thus, the present FE-SEM results can be regarded as evidence for the formation of porous structure. There is no remarkable dependency of crystal morphology on the mixing ratio of manganese oxide and graphene oxide, confirming homogeneous distribution of manganese oxide.
Yu Ri Lee, Min-Sun Song, Kyung Min Lee, In Young Kim and Seong-Ju Hwang

and graphene oxide. The observed porous morphology of the present nanocomposite is quite different from the non-porous morphology of the pristine $K_{0.45}MnO_2$ material. \(^{26}\) This result provides strong evidence for the usefulness of reassembling with reduced graphene oxide nanosheets in increasing the porosity of metal oxide.

The elemental distribution of manganese ions in the nanocomposites is examined with EDS elemental mapping. As can be seen clearly from Fig. 3, a uniform appearance of Mn signal is obviously discernible in the nanocomposite RMGO1 : 1, confirming the homogeneous distribution of manganese oxide in the present nanocomposite.

**FT-IR Spectroscopy**

The effect of heat-treatment on the chemical bonding nature of the graphene oxide component in the nanocomposites is examined with FT-IR spectroscopy. As plotted in Fig. 4, the FT-IR spectra of the as-prepared nanocomposites demonstrate several IR bands related to the carbon-oxygen bonds and $sp^3$ carbon-hydrogen bonds in the wave-number region of 900-1800 and 2900-3000 cm$^{-1}$, \(^{33,34}\) respectively. These spectral features indicate the presence of graphene oxide and TBA$^+$ ions, respectively. After the heat-treatment, all these peaks are markedly depressed, confirming the reduction of graphene oxide in the nanocomposite.
composites into the reduced graphene oxide and the removal of TBA\textsuperscript{+} cations.

**Mn K-Edge XANES Analysis**

The local structure and electronic configuration of manganese ions in the as-prepared nanocomposite MGO 1:1 and its calcined derivative RMGO 1:1 are investigated with Mn K-edge X-ray absorption near-edge structure (XANES) spectroscopy. Fig. 5 represents the Mn K-edge XANES spectra of the nanocomposites, compared with those of the pristine K\textsubscript{0.45}MnO\textsubscript{2}, the exfoliated MnO\textsubscript{2} nanosheets, MnO, MnO\textsubscript{2}, and β-MnO\textsubscript{2}. The as-prepared nanocomposite shows nearly identical edge position to those of exfoliated MnO\textsubscript{2} nanosheets, which are higher than that of the reference Mn(III)\textsubscript{2}O\textsubscript{3} but slightly lower than that of the β-Mn(IV)O\textsubscript{2}. This indicates that there is no significant change in the Mn oxidation state upon the nanocomposite formation with graphene oxide and the as-prepared nanocomposite possesses the mixed valent Mn(III)/Mn(IV) ions. After the heat-treatment, the as-prepared manganese oxide-graphene oxide nanocomposite displays a remarkable red-shift of edge position to the midway of the reference MnO and Mn\textsubscript{2}O\textsubscript{3}, indicating the reduction of Mn oxidation state to Mn(II)/Mn(III).

All the present manganese compounds including both the nanocomposites exhibit only a weak intensity for the pre-edge peaks P and/or P' corresponding to the dipole-forbidden 1s→3d transition.\textsuperscript{35-37} Since this transition is not allowed for the centrosymmetric octahedral symmetry, the observed weak intensity of these features confirms the stabilization of manganese ions in the octahedral symmetry in the nanocomposites with graphene oxide before and after calcination process. The main-edge peak B related to the dipole-allowed 1s→4p transition reflects sensitivity of the local atomic arrangement of manganese oxide.\textsuperscript{30-37} A sharp and intense peak B is observable for the layered manganese oxide consisting of edge-shared MnO\textsubscript{6} octahedra. Like the pristine K\textsubscript{0.45}MnO\textsubscript{2}, the as-prepared nanocomposite shows a sharp peak B, indicating the maintenance of layered manganate lattice after the composite formation. After the heat-treatment, this peak B becomes broad and weak, strongly suggesting a structural modification of layered manganese oxide component into non-layered manganese oxide phase.

**Electrochemical Measurements**

The electrode activity of the reduced graphene oxide-manganese oxide nanocomposites is tested by measuring the CV data of these materials with several electrolytes. The CV data of the nanocomposite RMGO 2:1 collected with the aqueous solutions of 0.2 M alkali metal sulfate are presented in the left panel of Fig. 6. The rectangular-type CV curves are observable for the present nanocomposite without any distinct redox peaks, showing its pseudocapacitance behavior. Overall features of the CV data are similar for the electrolytes of Li\textsubscript{2}SO\textsubscript{4} and K\textsubscript{2}SO\textsubscript{4}. A more severe distortion in the CV curve is observed for the Na\textsubscript{2}SO\textsubscript{4} electrolyte. In comparison with the Li\textsubscript{2}SO\textsubscript{4} and Na\textsubscript{2}SO\textsubscript{4} solutions, a larger specific
Yu Ri Lee, Min-Sun Song, Kyung Min Lee, In Young Kim and Seong-Ju Hwang

Capacitance can be obtained for the aqueous K$_2$SO$_4$ solution. In general, two mechanisms are responsible for the specific capacitance of metal oxide electrode; the surface adsorption/desorption and the intercalation/deintercalation of alkali metal ions. Due to the smaller hydration radius of potassium cation, this ion is advantageous in terms of the former mechanism. Conversely, in terms of the latter mechanism, the small ionic size of lithium ions is helpful in increasing the specific capacitance of manganese oxide. That the specific capacitance of the present nanocomposite is only slightly larger for the K$_2$SO$_4$ electrolyte than for the Li$_2$SO$_4$ electrolyte suggests that both the aforementioned mechanisms make contribution to the capacitance behavior of the present nanocomposites. Based on this result, the CV data of all the present nanocomposites are measured in the electrolyte of aqueous 0.2 M K$_2$SO$_4$ solution. As can be seen from the right panel of Fig. 6, the nanocomposite of RMGO 2 : 1 shows a higher electrochemical activity than the other nanocomposites.

Also the galvanostatic charge-discharge cycling is carried out for the reduced graphene oxide-manganese oxide nanocomposites. As illustrated in Fig. 7, the pseudolinear time-dependences of potential confirm the pseudocapacitance behavior of the present nanocomposites. From the present cycling data, the initial capacitance is estimated as 80 F g$^{-1}$ for RMGO 2 : 1, 77 F g$^{-1}$ for RMGO 1 : 1, and 25 F g$^{-1}$ for RMGO 1 : 2, respectively. There is no significant capacitance fading for initial several cycles. The present results of electrochemical measurement clearly demonstrate that the increase of reduced graphene oxide leads to the decrease of the specific capacitance of nanocomposite. This strongly suggests that the high content of reduced graphene oxide is not advantageous for improving the electrode performance of the nanocomposite. Compared with these nanocomposites, the pristine K$_{0.45}$MnO$_2$ delivers smaller capacitance of ~50 F g$^{-1}$, underscoring the benefit of hybridization in improving the electrode performance. The observed improvement of the specific capacitance of manganese oxide is attributable to the formation of porous structure during restacking of nanosheets.

**Conclusion**

In the present work, the porous nanocomposites composed of reduced graphene oxide and manganese (II,III) oxide are synthesized by mixing two precursor colloidal suspensions and heating the as-prepared nanocomposite. The calcined reduced graphene oxide-manganese oxide nanocomposites possess a porous morphology formed by the house-of-cards stacking of reduced graphene oxide nanosheets. The heat-treatment for the as-prepared nanocomposite induces the change of layered manganese oxide to non-layered manganese oxide with the reduced oxidation state of Mn(II)/Mn(III) and the formation of reduced graphene oxide. The present nanocomposites show pseudocapacitance behavior, indicating the applicability of these materials as electrode material of supercapacitor. Currently we are trying to apply the present synthetic strategy to other 2D nanostructured materials such as layered cobalt oxide, layered ruthenium oxide, etc.

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**References**