Rational design of electrochemically active polymorphic MnO$_x$/rGO composites for Li$^+$-rechargeable battery electrodes

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ABSTRACT

Electrochemical behavior of different MnO$_x$ @reduced graphene oxide (rGO) composites derived from a MnO$_2$/GO template are thoroughly investigated. As-prepared MnO$_2$/GO mixture is gradually converted to MnO$_2$/rGO and finally to Mn$_3$O$_4$/rGO composites under controlled post annealing conditions. The semispherical Mn$_3$O$_4$ crystalline compound anchored composite exhibits stable electrode performances, including both the Li$^+$ anode and the Li$^+$-air cathode catalyst, induced by the electrochemically favorable composite with an effective large contact area between the active materials and the electronic conductive rGO. It is such a meaningful to suggest the facile and controllable synthetic procedures for obtaining Li-rechargeable electrodes with a MnO$_x$ nanoparticle-incorporated composites for the highly reactive lithiation/delithiation electrochemical reactions.

1. Introduction

Overall research on developing novel electrode materials with high energy density is crucial to meet the rapid growth for the very recent Li-ion rechargeable battery industry. The on-going commercialized Li-ion batteries (LIBs) use graphite as for the anode owing to its high coulombic efficiency with long term cyclic retention, while with limited energy density due to the low theoretical charge/discharge capacity, ~372 mA h g$^{-1}$.

Various transition metal oxides have been considered for the promising electrode materials for monovalent alkali metal-ion and -air batteries [1–3]. Among the proposed transition metal oxides, low cost and environmentally mild Manganese oxides (Mn-O) are eligible for the various electrode materials owing to their high specific capacities with relatively lower electromotive force, equilibrium voltages of < 1.0 V, compared to other transition metal (Co and Ni etc) compounds.

Multivalent Mn$^{n+}$O ($\text{Mn}_2\text{O}_3$, Mn$_3$O$_4$ and Mn$_2$O$_3$) and diverse polymorphs (including $\alpha$, $\beta$, $\gamma$ and $\delta$ phases) have been widely investigated both for LIB anodes and cathode catalysts in Li-air batteries (LABs) to improve the electrochemical performance of Li$^+$-ion converted cell systems [4–7]. Moreover, the electrochemically active MnO$_x$ nanoparticles were also considered as for the cathode material for Li battery applications [8–11]. For cathodes the overall electrochemical reaction with Li$^+$ follows the insertion/deinsertion mechanism hence, designing high surface area and understanding of the nanoparticulate morphology during Li$^+$-insertion is very important rather than the chemical composition. Therefore, synthesis of nanometer-sized MnO$_x$ is of great potential for cathodic applications, owing to its high surface area and unique properties.

Unfortunately, like as the insulating nature (10$^{-8}$-10$^{-7}$ S cm$^{-1}$) of metal oxides, conventional MnO$_2$-based electrode materials exhibit rapid capacity cycle fading with irreversible volume change during the repetitive Li$^+$ migration. To overcome those bottlenecks, forming a hybrid composite combining with electrically conductive compounds such as 1-dimensional multiwall carbon nanotubes (MWCNT) and/or 2-dimensional graphenes is known as the representative strategy to develop the efficient electrode materials [12–15].

Those high surface area to volume ratio carbon compounds normally known as an “conductive” buffer media that both alleviate volume exchange and enhance the overall conductivity for the given metal oxide-based composite electrodes. Additionally, the incorporated carbon compounds are electrochemically reactive as well even at low voltages, which partially adds supplemental capacity that compensates for the dilution of the active phase. Among the numerous activate carbon compounds, sheet- or platelet-like graphene oxides (GOs) can fruitfully mitigate the structural deformation of the metal oxide-based...
composite electrodes during the overall reversible charge-discharge reactions with stable electrical conductive property [16–18].

Up to dates, much works has been done on the preparation of a specifically designed “electrochemically-active” MnOx and conductive GO composite electrodes followed by the electrochemical performances for application in LIBs and LABs. However, it is still noteworthy to provide an in-depth study for the comparison between different MnOx/carbon compounds with relation to the degree of freedom for designing “optimized” composite of MnOx/rGO and overall Li⁺ ion storage performance among the prevailing MnOx/carbon mixture composites.

Herein, we synthesize the morphology and crystal phase controlled MnOx/rGO composite electrodes, MnO2/rGO and Mn3O4/rGO, and evaluate their electrochemical behavior. As prepared MnO2/GO mixture is gradually converted to MnO2/rGO and finally changed to Mn3O4/rGO composite under specific annealings, with which we can visualize the overall Li⁺ charge/discharge conversion reaction with a complementary impedance spectroscopy analysis. This study provides a comparative analysis with a rational design for the electrode performance for the optimized chemical compositions, morphologies and electrochemical properties of multiphase metal oxide-based composite and to select the specific electrochemical properties for the given electrochemical reactions in view of the materials engineering.

2. Experimental

GO was prepared by oxidizing commercial graphite flakes (Sigma Aldrich) using the well-known Hummers method. MnO2 nanowires were synthesized by a microwave-assisted hydrothermal reaction (MARS6 230/60, USA). The detailed experimental procedures were described in our previous work [18]. MnOx/rGO composite was obtained following this; polyethyleneimine (PEI)-treated 0.1 g MnO2 nanowires were dispersed in deionized water (100 ml) followed by mixing thoroughly with same volumetric concentration of GO solution, which was sonicated for 20 min and collected by centrifugation at 25,000 rpm. The as-prepared composites were freeze dried and then heated under an Ar atmosphere at 300 ~ 500 °C for 2 h to get the phase pure MnO2/rGO and Mn3O4/rGO composites, respectively.

A CR2032 half coin cells using the given composites as for working electrode and a lithium metal as for counter electrode were prepared to check Li⁺ storage performance. The active material, MnO2/rGO or Mn3O4/rGO, was mixed with a carbon black conductive and polyvinylidene fluoride (PVDF, Kureha KF-1100) binder dissolved in N-methyl-2-pyrrolidone (Sigma Aldrich, 99.5%) in a weight ratio of 80:10:10. The mixture slurry was uniformly cast onto a copper foil and dried in a 120 °C vacuum oven overnight. The coin cell was assembled with the resulting working electrode, lithium metal, separator (Celgard 2400), and electrolyte (1 M LiPF6 in ethylene carbonate/diethyl carbonate). The galvanostatic charge-discharge capacity and cycling performance were measured at the given current densities using TOSCAT-3100 battery testing equipment (Toyo Co. Ltd). Electrochemical impedance spectroscopy (EIS) was performed by applying an AC signal from 0.01 Hz to 100 kHz with 5 mVpp using an impedance analyzer (Biologic, Netherland). Finally, the catalytic effect on the Li–O2 cathode for the given MnOx/rGO composite was investigated. The carbon-based paste was prepared by mixing 80 wt% “conductive carbon (Ketjen black) and a MnOx/rGO powder” with a 20 wt% PVdF binder followed by thorough mixing in a NMP solvent. The paste was cast on the SUS mesh and then vacuum dried at 120 °C for 12 h. The loading amount of the paste slurry was about 1 mg cm⁻² per electrode. The air-permeable 2032 coin cell was composed of a lithium metal (anode) and the as-prepared paste coated SUS mesh (cathode), which was separated by a glass-fiber. Lithium trifluoromethane sulfonamide (1 M) in tetra ethylene glycol dimethyl ether was used as the electrolyte. The cell was tested using the galvanostatic WBCS-3000 battery cycler (WonAtech) with an applied current density of 100 mA gtotal⁻¹ for 10 h.

X-ray diffraction patterns were recorded using a powder diffractometer equipped with Cu Kα radiation. Additionally, high resolution X-ray diffraction data of the powder samples were collected from the synchrotron facility at the Pohang Accelerator Laboratory, in the scanning range of 10.0 ≤ 2θ ≤ 130.5 with a step size of 0.02°. In order to extract structural parameters of the composites, Rietveld refinement was performed using GSAS package [19]. A split pseudo-Voigt function was employed to describe the profile shape and the background was fitted manually in the initial run of the refinement. After successfully fitting the graphene peaks, the manually drawn background was replaced with a polynomial of the first degree. The background coefficients, half width, zero point, asymmetry parameters for the peak shape, pseudo-Voigt, scale factor and unit-cell parameters were refined.
until a reasonable convergence was obtained. The crystal structure and surface morphologies were characterized by scanning electron microscopy (XL-30S FEG Scanning Electron Microscope, Philips) and high resolution transmission electron microscopy (JEM-2100F, JEOL).

3. Results and discussion

Fig. 1 presents the schematic experimental procedure for forming MnO2/rGO and Mn3O4/rGO composites by using the surface treated-MnO2 nanowire and graphene compounds. To get well-dispersed and uniform MnO2/rGO mixtures, PEI overcoated MnO2 nanowires anchored on GO sheets were established first, and then the resulting MnO2/GO mixtures were converted to the hierarchical MnO2/rGO and Mn3O4/rGO during the post-annealing process. Please note that the detailed experimental conditions with supplemental data for the MnO2 nanowires and MnO2/GO mixtures in our previous work [18]. Additionally, further enhancement of charge transfer kinetics induced by the PEI-induced interlayer in electrostatically assembled composite materials is also clarified through electrochemical impedance analysis in our work [20]. Thus, within the appropriate ambient/temperature conditions, we can successively acquire MnO2/rGO composites with the phase/morphology of MnO2 (active material) as well as the degree of the reduction of graphene oxide (conductive material), MnO2/rGO and Mn3O4/rGO, respectively.

Rietveld refinement of the MnO2/rGO composite is shown in Fig. 2. The broad peaks around 20 and 40° were assigned to the reflections from (002) and (100) planes respectively of the rGO, and the remaining sharper peaks were assigned to the tetragonal I4/m space group. Multi-phase refinement was employed to fit the component phases in the composite material. The broad rGO peaks were successfully fitted with a hexagonal space group P63mc, and a structural model belonging to I4/m space group was used to define the reflections from MnO2 phase. The successive refinement cycles gave reasonable convergence so that the \( R_W \) and the goodness of fit parameter (\( \chi^2 \)) assume 2.38% and 2.94%. The converged refinement parameters and the corresponding unit cell parameters of the MnO2 structure are shown in Table 1. From the unit cell parameter, the d-spacing of the graphene was calculated as 4.63 Å. This corresponds to the d-spacing of the reduced graphene oxide. In the Mn3O4/rGO composite, the broad peak corresponding to the (002) reflection of the reduced graphene was moved to a relatively higher 2θ value. On the other hand, the peak corresponding to the (100) reflection was not well resolved. A tetragonal space group I41/amd was used to index the MnO2 phase. The rGO present in the composite appeared to be more amorphous compared to that of MnO2/rGO composite. The refinement parameters were converged to reasonable values. The lattice parameters of Mn3O4 and the corresponding refinement parameters are tabulated in Table 1. The d-spacing of the graphene was calculated as 3.851 Å, indicating a highly reduced state of graphene in comparison to its counterpart in the MnO2/rGO composite. The high resolution TEM and SAED images for the corresponding MnO2 and Mn3O4 nanoparticles clearly exhibited the crystalline nature of MnO2 compounds (Fig. 2 insets). Thus, the MnO2/rGO composite was thoroughly converted to the spinel phase Mn3O4 anchored on rGO under a controlled synthetic procedure.

The phase analysis is well matched to the XRD results (sfig. 1) of which the two individual MnO compounds are crystalline MnO2 (JCPDS No. 044–0141) and Mn3O4 (JCPDS No. 080–0382) along with graphene peaks without any secondary phases. Thus, we can get the desired composition mixture compounds under the same conditions and directly compare the overall electrochemical performances, i.e., capacity retention, rate capability and coulomb efficiency, respectively.

We further explored the morphology for the nanoparticles and composites. As shown in Fig. 3, different shaped numerous nanoparticles anchored micron-scale layer-by-layer structure were clearly observed. Nanowire (similar to the pristine MnO2) shaped MnO2/rGO composites are well preserved, while semispherical Mn3O4 nanoparticle-anchored composites for the Mn3O4/rGO, respectively.

With further annealing conditions, only the morphology of the incorporated MnO2 nanoparticles were moderately changed from uniaxial to spherical one, while the 2D platelets (assuming the graphene oxide sheets) can still preserve the stable layer-by-layer frameworks. Thus, we can expect that the phase/structure controlled MnO2/rGO composite electrodes might be effective to facilitate rapid Li+ ion movement within the repetitive cyclic reactions.

Table 1

<table>
<thead>
<tr>
<th>Formula</th>
<th>MnO2</th>
<th>Mn3O4</th>
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</thead>
<tbody>
<tr>
<td>Radiation type</td>
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<td>Synchrotron</td>
</tr>
<tr>
<td>2θ range (degree)</td>
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<td>10–100</td>
</tr>
<tr>
<td>T/K</td>
<td>295</td>
<td>295</td>
</tr>
<tr>
<td>Symmetry</td>
<td>Tetragonal</td>
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</tr>
<tr>
<td>Space group</td>
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<td>I41/amd</td>
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<tr>
<td>z</td>
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<td>4</td>
</tr>
<tr>
<td>a=b=Å</td>
<td>9.9042(6)</td>
<td>5.7750(6)</td>
</tr>
<tr>
<td>c=Å</td>
<td>2.85938(8)</td>
<td>9.4586(20)</td>
</tr>
<tr>
<td>V/Å³</td>
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<td>315.45(7)</td>
</tr>
<tr>
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<td>3.93%</td>
<td>4.23%</td>
</tr>
<tr>
<td>Rwp</td>
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<tr>
<td>x²</td>
<td>2.94</td>
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</table>

Fig. 2. Synchrotron diffractions and corresponding HR-TEM images with SAED patterns of (a) MnO2/rGO and (b) Mn3O4/rGO composites. Dots represent the observed intensities, and the solid line is calculated ones. A difference (obs. – cal.) plot is shown beneath. Panel on the top of the plot shows the calculated Bragg’s positions of the corresponding rGO and MnO2 crystalline phases.
The galvanostatic charge-discharge capacity and cycling performance were measured at the given current densities. Based on the previous works, the reversible conversion reaction for the given MnOx/rGO may induce the following electrochemical reactions:

\[
\begin{align*}
\text{MnO}_2 + 2\text{Li}^+ + 2e^- & \rightleftharpoons \text{MnO} + \text{Li}_2\text{O} \quad (1-1) \\
\text{Mn}_3\text{O}_4 + 2\text{Li}^+ + 2e^- & \rightleftharpoons 3\text{MnO} + \text{Li}_2\text{O} \quad (1-2) \\
\text{MnO} + 2\text{Li}^+ + 2e^- & \rightleftharpoons \text{Mn} + \text{Li}_2\text{O} \quad (2)
\end{align*}
\]

It is clear that the specific capacities for the MnO2/rGO composite electrodes were much higher than the other one during the successive electrochemical reactions as shown in charge/discharge profiles, Fig. 4(a). As shown in Fig. 4(b), however, the capacity change with cycles for the given composite electrodes was very similar to each other, which gradually increased up to ~35 cycles then decreased in the subsequent discharge/charge cycles and finally leads to a stable capacity retention at 970 mA h g\(^{-1}\) for MnO2/rGO and 375 mA h g\(^{-1}\) for Mn3O4/rGO.

Although the absolute capacity values for Mn3O4/rGO both initial states and even at 100 cycles was substantially lower than the MnO2/rGO, the charge/discharge capacity and coulomb efficiency retention were stable enough, which suggested an ideal complex structure formation for Li\(^+\) storage behavior.

To support the characteristic cycle behavior for the given MnOx/rGO electrodes, we have done the comparative analysis between the capacity retention and the Li\(^+\) kinetics within the cyclic electrochemical reaction. There are many works regarding the significant increase/decrease in capacity of transition metal oxides-based composite electrodes upon cycling. Generally, it is often attributed to the different activation process of the outer shells and inner core of active materials, the increase in lithium accessibility due to the morphology of the electrode material, or a mere hierarchical structure [21–23].

With EIS results, we can realize the constituent resistance components (charge transfer and SEI formation etc.) for the given MnOx/rGO composites. It might be evaluated by the degree of structural relaxation between the active (MnOx) and conductive (rGO). Up to 10 cycles, as shown in Fig. 5(b), the EIS spectra exhibit two prominent semicircles positioned at high frequency region with a straight line at low frequency one, of which the former one related to the charge-transfer mobility (R\(_2\)) and the other one is the mass transfer region (R\(_3\)). Note that the first semicircle corresponded to the SEI formation on the composite electrode within the 20 mHz-10 Hz region [24,25]. With subsequent cycles, after 20th and 40th discharge reactions, the EIS curves substantially changed to a singular semicircle with much decreased resistances especially in high frequency range. It was interesting to realize the decreased impedance for the as-synthesized MnOx/rGO composite electrodes compared to the gradually increased EIS curves of the conventional anode materials in the post-annealed rGO electrodes that we measured.

The eventually decreased charge transfer resistance represents stimulating Li\(^+\) ion mobility induced by the excellent “electrical” contact between the active center, MnOx, and conductive layers, rGO. This is in good agreement with the fact that the structural relaxation favored to the optimized electrochemical reactions for the composites electrodes during the repetitive cycles enhanced the electrochemical reaction within the composite electrode material, as reported previously [22,25,26].

Moreover, the electrochemical reaction using the Mn3O4/rGO composite electrode is more favorable to the repetitive cyclic reactions induced by the effective formation; well-stacked rGO platelets incorporated with Mn3O4 semispherical particles, which facilitate overall charge transfer kinetics.

Both MnO2 and Mn3O4 are suggested as for the promising oxygen
catalysts at Li-air battery cathode [4,27,28]. Thus, finally we have measured the electrocatalytic reaction for the given MnOx/rGO composite. The discharge capacity measured at first galvanostatic discharge reaction, Li + O2(g) → Li2O(s), are presented in Fig. 6(a). The catalytic reaction for the formation of lithium peroxides using the Mn3O4/rGO are more effective than other electrode compositions, ∼5600 mA h g−1 for Mn3O4/rGO, ∼5000 mA h g−1 for MnO2/rGO and 2600 mA h g−1 for Ketjen Black only, respectively. It is well matched to the crystallinity for the lithium peroxides overcoated at the given air cathode; the Li2O XRD peaks (Fig. 6(b)) for the Mn3O4/rGO incorporated cathode are broader than that of the MnO2/rGO cathode, which finally leads to the prolonged cyclic reaction with oxygen gas [29]. Those results were similar to the enhanced charge/discharge performance, which facilitated the formation and decomposition of the LiOx within the MnOx uniformly interdispersed MnOx/rGO stacked framework and thus reduces the detrimental pore clogging. Consequently, the MnOx/rGO foam maintained a more stable reversibility than other MnOx/GO composites during discharge/charge, thereby supporting the reversible formation/decomposition of LiOx by-products.

4. Conclusions

Phase transition with corresponding electrochemical behavior of the different MnOx/rGO composites, MnO2/rGO and Mn3O4/rGO, are thoroughly investigated. Within the controlled annealing conditions, as-prepared MnOx/GO mixture was successively changed to MnO2/rGO and finally converted to Mn3O4/rGO composites, of which the phase variable “electrochemically” active nanoparticles anchored on “electrically” conductive media in a sequence. We can realize the abrupt capacity change behavior in the initial stages (up to 40 cycles), which normally occurred in the metal oxide nanoparticle/graphene composite electrode via a comparative electrochemical impedance analysis. Although the absolute capacity value for the Mn3O4/rGO anode was substantially lower than that of the nanowire MnO2 anchored on rGO, the stable capacity retention under variable current density conditions and the Li⁺ → LiOx(s) conversion reaction at the Li-air cathode suggested an improvement in the reversibility of the electrode reactions and catalytic activity.

The observed enhancement in performance of electrode using Mn3O4/rGO composite is attributed to the reduced charge transfer resistance across the MnOx/rGO interfaces as well as the well-incorporated MnOx nanoparticles within the much reduced GO interlayers, which effectively stimulate both “electrochemical reaction” and “electrical conduction” for the given composites.

The proposed synthesis with a rational design and forming phase variable composites in a consecutive procedures can be widely used to acquire other multicomponent oxide hybrid compounds with complex mixtures designated electrode performance what we want to use.

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