Nanoscale MnO mildly expanded graphite (MnO/MEG) composites were synthesized by a facile hydrothermal method combined with a subsequent self-reduction process using MEG as the raw material. The physicochemical and electrochemical properties of this novel MnO/MEG composite were characterized by X-ray diffraction, scanning electron microscopy, galvanostatic charge/discharge tests, cyclic voltammetry, and electrochemical impedance spectroscopy measurements. MnO/MEG exhibits excellent electrochemical performance for which the reversible capacity is as high as 931 mAh g$^{-1}$ at 0.3 C after 450 cycles, which can be attributed to nanoscale MnO on MEG and self-developed graphene during the charge/discharge process.

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In this study, we prepared nanoscale MnO/mildly expanded graphite (MnO/MEG) composites by a facile hydrothermal method combined with a subsequent self-reduction process. MEG acts as both the base material and also the reducing agent. As expected, the hybrid MnO/MEG electrode exhibits excellent electrochemical properties, which can be attributed to the synergetic effect of MEG and MnO nanocrystals. It was also found that MEG can be self-developed to graphene with high energy density in charge/discharge process.

Experimental

MEG preparations.—MEG was synthesized using a modified Hummer’s method. First, graphite powder (3 g) and NaNO$_3$ (0.25 g) were added to 40 mL concentrated H$_2$SO$_4$ in an ice bath and stirred for 30 min. 0.3 g KMnO$_4$ was then added and the mixture was stirred for another 2 h. After this, 40 mL deionized water was added and the mixture was kept at 100°C for 30 min. 80 mL H$_2$O$_2$ was then added to the mixture and stirred for another 30 min to further oxidize the graphite. After cooling to 40°C, the produced precipitate was then collected by filtration, washed several times with HCl (5%) solution and deionized water, and dried in an oven at 60°C for 12 h. Subsequently, the products were calcinated at 900°C for 3 h under an N$_2$ atmosphere to obtain precursor. Finally, the precursor was reduced by hydrazine hydrate in oil bath (100°C for 2 h), and the MnO was obtained after filtrating, washing, and drying.

MnO/MEG composites preparation.—After 0.6 mmol KMnO$_4$ (AR) was dissolved in 30 mL deionized water, 0.2 g MEG was added and stirred for 10 min. Then, the obtained homogeneous amaranthine suspension was transferred into a 50 mL Teflon-lined autoclave and heated at 150°C for 12 h. After cooling to room temperature, the precipitate was filtered, washed, and dried at 60°C overnight. Finally, the product was ground to powder and sintered at 550°C for 3 h in flowing nitrogen gas. The final product can be referred as MnO/MEG composite.

Materials characterization.—The phase identification of the obtained samples was performed by powder X-ray diffraction (XRD, Rigaku Ultima IV) using Cu-ka radiation ($\lambda$ = 1.5406 Å). Diffraction patterns were obtained over the range of 20 between 10° and 90° in steps of 8° • min$^{-1}$. The morphologies were examined using a scanning electron microscope (SEM, JSM-7500F, JEOL) and a transmission electron microscope (TEM, JEM-2100, JEOL). The Raman spectrum was performed on Raman spectrometer (LabRAM HR8000, Horiba JobinYvon). To examine the content of MnO, thermogravimetry (TG) experiments were performed in air flow from 20 to 1000°C using a simultaneous thermal analyzer (STA449F5, Netzsch).

Electrochemical measurements.—First, the working electrodes were fabricated by coating a slurry on a copper foil, the slurry containing a mixture of active material (80 wt%), acetylene black (10 wt%), and polyvinylidene fluoride (PVDF, 10 wt%) dissolved in N-methyl-2-pyrrolidinone. The coated copper foil was cut into disk electrodes (14 mm diam) and dried at 120°C for 12 h in vacuum. The electrochemical performance of the active material was studied by measuring the assembled CR2025 coin cells which used pure lithium foil as the counter and reference electrodes, Celgard 2400 as the separator, and 1 M LiPF$_6$ in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (v/v = 1:1) as the electrolyte. The test cells were assembled in an argon-filled dry box (MIKROUNA, Super 1220/750).
Figure 1. (a) XRD patterns and (b) Raman spectrum of MEG and MnO/MEG.

The galvanostatic charge/discharge measurements were carried out using a Land Battery Measurement System (LAND CT2001A, China) in a fixed voltage range of 0.001–3.000 V vs. Li/Li\(^+\) at room temperature. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were performed using an electrochemical working station (CHI614C, China) at room temperature. CV curves were monitored at a scanning rate of 0.1 mV s\(^{-1}\) within a voltage range of 0–3 V; EIS spectra were obtained in a frequency range from 0.01 Hz to 100 kHz.

Results and Discussion

Figure 1a shows the XRD patterns of MEG and MnO/MEG composites. For MnO/MEG, the diffraction peaks located at 42.2°, 44.4°, 54.5°, 59.7°, 77.2°, 83.2°, and 86.8° (see the inset of Fig. 1a) can be indexed as the (100), (101), (004), (103), (110), (112), and (006) faces of graphite (JCPDS, No. 41-1487). The other diffraction peaks at 34.9°, 40.5°, 58.7°, 70.2°, and 73.8° match well with the (111), (200), (220), (311), and (222) faces of MnO (JCPDS, No. 07-0230). This indicates that MnO particles may form on the surface of MEG\(^{16,17}\) or insert in the layers of carbon in graphite\(^{27,28}\) during the reduction of MnO\(^{x}\) in the sample preparation, the MnO content in the MnO/MEG composite evaluated by TG is 16.4 wt%. Moreover, it can be observed that the graphite peak at 26.5° shifts to the lower 2\(\theta\) side in the enlarged patterns of Fig. 1a. The effect can be attributed to the insertion of nanoscale MnO into carbon layers of graphite, leading to the increase of interlayer distance.

Raman spectra were performed to investigate the structural changes from MEG to MnO/MEG composite (Fig. 1b). The Raman scattering peak observed at \(\sim 637\) cm\(^{-1}\) should correspond to the Mn-O vibration mode.\(^{29,30}\) The peak at \(\sim 1360\) cm\(^{-1}\) (D band) was attributed to the sp\(^3\) hybridized C-C bonds that stemmed from the distorted hexagonal lattice in the graphite layers, and the peak at \(\sim 1580\) cm\(^{-1}\) (G band) originated from the in-plane vibrations of sp\(^2\) hybridized C-C bonds. The intensity ratio of D and G bands (I\(_D\)/I\(_G\)) is usually used to evaluate the graphitization degree of carbon.\(^{21,31}\) The lower I\(_D\)/I\(_G\) ratio, the higher the graphitization degree of the residual carbon is. The I\(_D\)/I\(_G\) ratio of MEG (0.12) is much lower than that of MnO/MEG (0.21), which demonstrates that the disorder degree of the planes and the exfoliation of MEG aggravate during the forming process of MnO/MEG composites. Consequently, the non-graphitic carbon may possess more Li\(^+\) storage sites than graphitic carbon.\(^{21,32}\)

The morphologies of the MEG (a, b) and MnO/MEG (c, d) composites were shown in Fig. 2. The SEM images of MEG (Figs. 2a and 2b) clearly display smooth surfaces with some folds and cracks. After the reaction with KMnO\(_4\) and the subsequent self-reduction and calcination, the surface of MnO/MEG composites (Figs. 2c and 2d) becomes vague, the folds and cracks of MnO/MEG are increasingly obvious, the MnO particles (\(\sim 50\) nm) are uniformly distributed on the surface of MEG. Such cracks caused by MnO insertion could provide more space for Li\(^+\) storage and migration during charge/discharge process.\(^6\)

Cycling performances of MEG and MnO/MEG composites are compared in Fig. 3. It is obvious that the initial reversible capacity of MnO/MEG is 475 mAh g\(^{-1}\) at 0.3 C and it reaches 931 mAh g\(^{-1}\) after 450 cycles, which is 250% of the theoretical capacity of graphite (372 mAh g\(^{-1}\)) and much higher than that of MnO (756 mAh g\(^{-1}\)). The initial capacity of MEG is only 381 mAh g\(^{-1}\) at 0.3 C. The reason for the enormous increase of capacity can be summarized as the following: first, the MEG matrix provides an efficient electron conductivity network, which can greatly improve the capacity retention, and second, MEG acts as a barrier to effectively suppress the
aggregation of MnO particles and accommodate the volume changes of MnO particles during Li$^+$ insertion/extraction. It is of interest that the capacity of MnO/MEG increase gradually with cycling (Fig. 3), as observed previously by other groups for nanostructured Mn-based oxides.16,33,34

Figure 4 shows the charge/discharge profiles of MnO/MEG composite for cycles 1, 2, 200, 450 at 0.3 C (Fig. 4). It is clearly seen that the potential platform (< 0.2 V) associated with graphite becomes inconspicuous with cycling and disappears after 200 cycles. This phenomenon may be due to the huge volume changes of MnO commonly existing in intercalation compound during the charging/discharging process. It is the volume changes that promote the stripping of graphite layers to form a structure similar to graphene, 35 which is beneficial to capacity improvement of the MnO/MEG composite.

To further understand the stripping of graphite layers of MnO/MEG with cycling, SEM images of MnO/MEG electrode after 200 and 300 cycles at 0.3 C are shown in Figs. 5a and 5b. It is observed that MEG was further stripped after 200 cycles, but MnO particles were still attached on the surface of MEG (Fig. 5a). After 300 cycles, the defect was further amplified so that many holes were generated and the surface of graphite was stripped to fold graphite plates. Meanwhile, the MnO particles located on MEG almost disappeared (Fig. 5b). It is clearly seen that such a defect caused by stripping might be related to the volume effect of MnO in the charge/discharge process. The structural changes of MnO/MEG electrode after 450 cycles were further confirmed by XRD (Fig. 5c) and TEM (Fig. 5d). Apart from the diffraction peaks related to graphite, XRD patterns do not exhibit diffraction peaks related to MnO after the first cycles. Disappearance of MnO peaks indicates the transformation from crystallized particles into amorphous feature. In addition, the sharp (002) diffraction peak of graphite is widened after 450 cycles, thus indicating self-developed graphene from MEG.

To study the rate capability and cycle stability of the MnO/MEG composites, rate and cycling (at 3 C) curves are shown in Fig. 6. As seen in Fig. 6a, the reversible capacity of MnO/MEG reached 435, 405, 357, 300, 260, 220, and 155 mAh g$^{-1}$ at rate of 0.5, 1, 2, 3, 4, 5, and 8 C, respectively. The capacity was recovered to 463 mAh g$^{-1}$ when the rate was returned to 0.5 C. Here, considering that the penetration of electrolyte into the electrode and the formation of solid electrolyte interphase (SEI) can be completed in the initial few cycles, we tested the MnO/MEG composite at 0.5 C in the first three cycles, and then changed at 3 C. The specific capacity of the composite is about 370 mAh g$^{-1}$ and the capacity retention ratio is up to 83% after 700 cycles (Fig. 6b), indicating excellent rate capability and cycling stability for the MnO/MEG composite.

To further understand the electrochemical behavior of both samples, Fig. 7 shows representative CV curves of the MEG and MnO/MEG composites at a scanning rate of 0.1 mV s$^{-1}$ in the voltage range of 0–3 V. It is apparent that the reduction peaks (< 0.2 V) in both CV curves of MEG and MnO/MEG are very similar, which mainly belong to MEG (Figs. 7a and 7b). One small peak was observed at 0.7 V, but then disappeared in the subsequent cycles, corresponding to the irreversible reduction of electrolyte and the formation of SEI layer.36

In Fig. 7b, there was a noticeable reduction peak near 0.25 V in the
first cathodic sweep, which corresponds to the reduction of Mn$^{2+}$ to metallic Mn$^0$ ($\text{MnO}_2 + 2\text{Li}^+ + 2e^- \rightarrow \text{Mn} + \text{Li}_2\text{O}$). However, the lithiation potential in the second and following cycles ($\sim 0.5$ V) was higher than that in the first cycle ($\sim 0.25$ V), mainly due to improved kinetics and partially to the deviation of the formation energy of the reactants from the products after the first insertion.$^{15,16,36}$ Moreover, the anodic peak at about 1.3 V corresponds to the oxidation of Mn$^0$ to Mn$^{2+}$.

The EIS for the MEG and MnO/MEG composites are shown in Fig. 8. All EIS spectra are composed of a small intercept in the high-frequency region, a depressed semicircle in the medium-frequency region, combining with an inclined line in the low-frequency region. Both EIS curves were fitted by an equivalent circuit composed of “$R(C(R))(C(RW))$” using the ZView program, and the fitting results are shown in Table I. Among them, $R_e$ represents the total resistances of electrolyte, electrode, and separator. $R_f$ and $C_f$ are the resistance and capacitance of the SEI film, $R_{ct}$ and $C_{dl}$ are the charge-transfer resistance and double-layer capacitance, respectively. $W$ is the Warburg impedance arising from the semi-infinite diffusion of the lithium ions in graphite electrode.$^{38}$ The smaller the diameter, the lower the charge-transfer resistance is. From Fig. 8 and Table I, it is found that the fresh cell of MnO/MEG shows the lower charge-transfer resistance ($R_{ct} = 29.54 \Omega$) and resistance of SEI film ($R_f = 7.60 \Omega$), which confirms that MnO/MEG presents the faster kinetics of the electrochemical reactions. It is also observed that the charge-transfer resistance (11.22 $\Omega$) of the sample for the tenth cycle is much smaller than the fresh cycle (29.54 $\Omega$). To further study the gradually increasing capacity of MnO/MEG with cycling, the Li-ion diffusion coefficient ($D_{Li^+}$) was calculated according to the following equations$^{17,31}$

$$D_{Li^+} = \frac{R^2T^2}{2A^2n^4F^4C_{Li}^2\delta^2}$$

where $R$ is the gas constant, $T$ is the absolute temperature, $A$ is the surface area of the electrode, $n$ is the number of electrons per molecule during oxidation, $F$ is the Faraday constant, $C_{Li}$ is the concentration of lithium ion, and $\delta$ is the Warburg coefficient. The real part of the impedance, $Z'$, is given by$^{17,31}$

$$Z' = R_e + R_{ct} + \delta\omega^{-1/2}$$

where $\omega$ is the angular frequency in the low-frequency region. Both $R_e$ and $R_{ct}$ are kinetics parameters independent of frequency, so $\delta$ is also the slope for the plot of $Z'$ vs. the reciprocal square root of the lower angular frequencies ($\omega^{-1/2}$). To obtain the Warburg coefficient ($\delta$), the linear fitting of $Z'$ vs. $\omega^{-1/2}$ in the low-frequency region of MnO/MEG sample is shown in Fig. 8b. As listed in Table I, the Li$^+$ diffusion coefficient of MnO/MEG gradually increased with cycling, whereas

![Figure 7. CV profiles of the as-prepared samples.](image1)

![Figure 8. (a) EIS curves for fresh and the 10th cycles, and (b) relationship between $Z'$ and $\omega^{-1/2}$ in the low frequency region of MEG and MnO/MEG.](image2)
the Li\(^+\) diffusion coefficient of MEG decreased. Based on refinement results, it is apparent that the \(D_{Li^+}\) of MnO/MEG (3.23 \(\times\) \(10^{-13}\) cm\(^2\) s\(^{-1}\)) is far higher than that of MEG (1.97 \(\times\) \(10^{-13}\) cm\(^2\) s\(^{-1}\)) after 10 cycles. The increased \(D_{Li^+}\) of MEG/MnO further indicated that the improvement of activation and reaction kinetics upon cycling. The EIS results are also in good agreement with the results of electrochemical performance tests.

Conclusions

Nanoscale MnO/MEG composites were synthesized by facile hydrothermal method combined with a subsequent self-reduction process followed heat-treatment. The MnO/MEG composites exhibit excellent cycling stability and good rate capability, which benefit from the presence of conductive MEG and a short transportation length for both lithium ions and electrons. Moreover, the as-formed hybrid nanostructure of MnO/MEG may help achieving fast kinetics of conversion reactions. Importantly, the reconstruction of MnO inserted in the layers of MEG also facilitates the self-development of graphene with high energy density during repeated charge/discharge process.

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