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Nanocomposites of Reduced Graphene Oxide for Energy Storage Applications

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A well-crystallized and nano-sized Metal oxide/reduced graphene oxide composite material for lithium ion batteries has been successfully synthesized. The nano-sized metal oxide particles were evenly dispersed on the reduced graphene oxide template without any agglomeration, which allows the inherent high active surface area of individual metal oxide nano-particles in the composite. These unique structural and morphological properties of metal oxide on the highly conductive reduced graphene oxide sheets in the composite enable achieving the high specific capacity, and excellent high rate capability and stable cycling performance. an analysis of the cyclic voltammogram data revealed that a large surface charge storage contribution of the metal oxide/reduced graphene oxide nanocomposite plays an important role in achieving faster charge/discharge.

Keywords: Lithium Ion Battery, Metal Oxide, Reduced Graphene Oxide, Nanocomposite.

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1. INTRODUCTION

Reduced graphene oxide (RGO) is expected to bring about a breakthrough in many applications including electrochemical energy storage devices due to its large specific surface area, high electrical conductivity, its chemical and mechanical properties. One obvious challenge would be to utilize the 2D carbon nanostructure with regard to its large specific surface area and edge sites for the potential application in energy storage devices. RGO would be an excellent electrode materials and templates for the preparation of nanocomposites with metal oxides for electrochemical capacitor(EC) and Li ion battery applications [1, 2, 3].

Metal oxide/RGO nanocomposites are also of considerable interest for electrochemical energy storage applications owing to their unique electrical, chemical, and electrochemical properties. These excellent properties of metal oxide/RGO nanocomposites are generated from synergistic combination of RGO with metal oxide on the nanometer scale. Pseudocapacitive reaction of metal oxide is likely to occur only at the surface or a very thin surface layer of the oxide. Therefore, metal oxide/RGO nanocomposites, where metal oxide forms only on the surface of RGO on the nanometer scale with a control over particle size, particle size distribution, coating layer thickness, thickness uniformity and loading amount of metal oxide on RGOs, are expected to improve both high power and high energy properties for energy storage applications.

2. EXPERIMENTAL

2.1 Material preparation

A MnO_2/RGO nanocomposite was first prepared by a direct redox reaction between RGO and MnO_4^- in aqueous solution. RGO nanosheets were used as a high surface area template for the selective heterogeneous nucleation and growth of MnO_2.[1] This MnO_2/RGO nanocomposite was then allowed to react with LiOH aqueous solution for conversion to the $LiMn_2O_4$/RGO nanocomposite under MAH conditions.

2.2 Material Charaterizations

X-Ray diffraction (XRD) patterns of the LMO/RGO nanocomposite were measured at the beamline X7B of the National Synchrotron Light Source at Brookhaven National Laboratory. The wavelength used was 0.3184 Å. The sample (5–10 mg) was loaded into a glass capillary with a diameter of 0.5 mm. Two-dimensional powder patterns were collected with an image plate detector and the powder rings were integrated using the FIT2D code. The lattice parameter was determined by a Rietveld analysis using the general structure analysis system (GSAS) program The instrumental parameters (Thompson–Cox–Hastings profile coefficients) were derived from the fit of a LaB_6 reference pattern. Transmission electron microscopy (TEM) imaging was performed on a JEOL JEM2100F TEM operated at 200 kV.

The electrochemical properties were investigated using a three-electrode electrochemical cell , with two lithium foils as counter and reference electrodes at room temperature. The working electrode was prepared by mixing 85 wt % active material ($LiMn_2O_4$/RGO nanocomposite, $LiMn_2O_4$), 10 wt % acetylene black and 5 wt % polyvinylidene fluoride dissolved in *N*-methylpyrrolidone as a binder. The slurry mixture was coated on a titanium foil (99.7 % purity, Aldrich) and then dried at 100 °C for 24 h. Each working electrode with a 1×1 cm^2 area contained 1–2 mg of the dried slurry. The charge–discharge tests and cyclic voltammetry were carried out at between 3.5 and 4.5 V (*vs.* Li/Li^+) using a potentiostat/galvanostat (VMP2, Princeton Applied Research). The electrolyte used was 1 M $LiPF_6$ dissolved in a mixture of ethyl carbonate (EC) and diethyl carbonate (DEC) at a volume ratio of 1 : 1. The specific capacity was calculated based on the weight of the $LiMn_2O_4$ in the $LiMn_2O_4$/RGO nanocomposite electrode . (A 1 C rate corresponds to a current rate of 148 mA g^{-1}, which in the ideal case gives complete discharge in 1 h, based on the 73 wt% $LiMn_2O_4$ in the $LiMn_2O_4$/RGO nanocomposite).

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3. RESULT AND DISCUSSION

Fig. 1 shows the X-ray diffraction (XRD) pattern of the $LiMn_2O_4$/RGO nanocomposite (73 wt. % of $LiMn_2O_4$ in the $LiMn_2O_4$/RGO nanocomposite). All peaks could be indexed based on the cubic spinel $LiMn_2O_4$ structure (space group:Fd-3m). Rietvelt refinement was performed using this structure and afforded an excellent fit, indicating the formation of well-crystallized spinel $LiMn_2O_4$ phase on the RGO template without any impurity phase. The refined lattice constant a (8.2134 ± 0.0002 Å) was slightly smaller than that of bulk stoichiometric $LiMn_2O_4$ (a = ~ 8.235 Å), which was attributed to either the slightly lithium-rich stoichiometry or the nano-size effect of the $LiMn_2O_4$ formed on the RGO template. The (002) peak of RGO was very weak, implying that the $LiMn_2O_4$ nanoparticles deposited on the RGO surface might prevent the restacking of the RGO sheets.

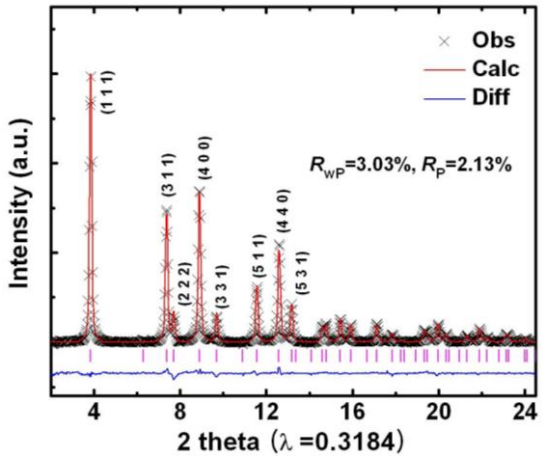

Fig. 1 – The Rietveld refinement of the spinel $LiMn_2O_4$/RGO nanocomposite materials

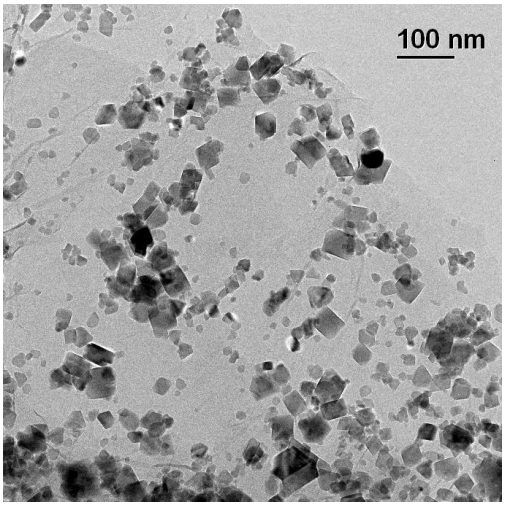

Fig. 2 – Low high-magnification TEM images of the spinel LiMn2O4/RGO nanocomposite materials

Transmission electron microscopy was used to investigate the morphology of the $LiMn_2O_4$/RGO nanocomposite material. Fig. 2 clearly shows the good dispersion and uniform coverage on the RGO nanosheets of the $LiMn_2O_4$ nanoparticles of size 10-40 nm.

Fig. 3 shows a cyclic voltammogram (CV) of the $LiMn_2O_4$/RGO nanocomposite electrode in an EC/DEC electrolyte of 1M $LiPF_6$ at increasing potential scan rate from 1 mVs^{-1} to 10 mVs^{-1}. The electrodes were fabricated by slurry casting of 85 wt. % active material ($LiMn_2O_4$/RGO nanocomposite), 10 wt. % acetylene black, and 5 wt. % PVDF binder dissolved in NMP solvent. The CV plot showed the typical shape of spinel $LiMn_2O_4$ with two pairs of well-separated current peaks in the 4V region. The two pairs of current peaks in the CV suggest that the lithium ions were extracted from and inserted into the spinel structure by a two-step process, which was in good agreement with those of typical well-crystallized spinel $LiMn_2O_4$

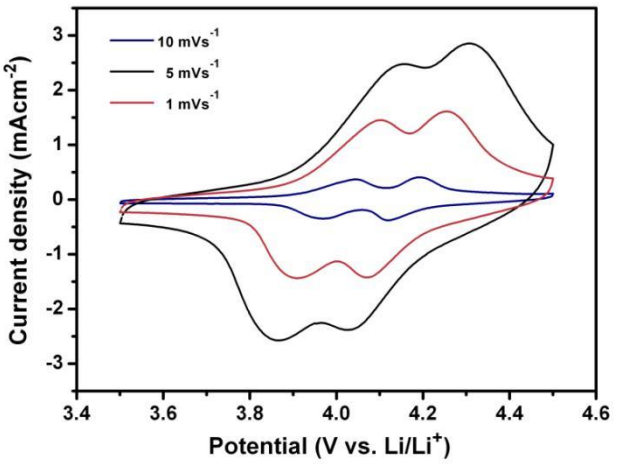

Fig. 3 – Cyclic voltammogram of the LiMn2O4/RGO nanocomposite electrode (CV; scan rate: 1 mVs^{-1} ~ 10 mVs^{-1})

The two initial current peaks of the CV at 0.1 mVs^{-1} were well distinguishable with increasing potential scan rate up to 10 mVs^{-1}, suggesting a good high rate capability for the $LiMn_2O_4$/RGO nanocomposite. This result is further verified by the charge/discharge curves at different C-rates. The rate performance of $LiMn_2O_4$/RGO was excellent, showing a capacity retention of 85 % at 50 C-rate and 74 % at 100 C-rate, compared with the specific capacity of 137 $mAhg^{-1}$ at 1 C-rate. A comparison of the rate performance of the $LiMn_2O_4$/RGO nanocomposite with data from the literature further supported its excellent rate capability.

4. CONCLUSION

A well-crystallized and nano-sized spinel $LiMn_2O_4$/RGO nanocomposite cathode material for high rate lithium ion batteries was successfully synthesized by a MAH method. Combined use of microwave irradiation and graphene as a template enabled the quick synthesis of a spinel $LiMn_2O_4$/RGO nanocomposite material with high crystallinity and ordered structure while maintaining a well-dispersed, nano-particular shape at very low temperature. This unique structural property of the $LiMn_2O_4$ in the nanocomposite supported a high specific capacity of 137 $mAhg^{-1}$ at 1 C-rate and an excellent rate performance.

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